A Comparative Study on Chiral and Racemic 12-Hydroxyoctadecanoic Acids in the Solutions and Aggregation States: Does the Racemic Form Really Form a Gel?

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Chiral and racemic forms of the title compound (12HOAs) were reinvestigated. Gels formed separately from D- and L-12HOAs became a solution containing crystallites on maintaining contact, confirming that DL-12HOA forms no gel, contrary to several reports published over more than ten years, which stated that DL-12HOA formed a gel (for example, P. Terech et al., *Langmuir* **1994**, *10*, 3406). The powder X-ray diffraction pattern of D-12HOA was different from that of DL-12HOA and the simulated patterns of two crystal structures of DL-12HOA. ^{13}C NMR spectroscopy for solutions of C_6D_6 showed significant difference in the concentration dependence of the low-field shifts at the carboxyl C due to hydrogen-bond formation. Analysis based on multiple equilibria among monomer, dimer, and tetramer was successfully applied to the behavior of D-12HOA, but not to that of DL-12HOA. For DL-12HOA, a modified model including hexamer was applied. It is concluded that association of dimers to tetramers and higher aggregates is more favorable in the DL-12HOA solution than in the D-12HOA solution and that D- and L-12HOA molecules recognize each other even in a dilute solution (lower than 2 mmol L^{-1}) of DL-12HOA. Different NMR spectra were also observed in the solid state.

Chiral recognition is a fundamental problem in chemistry. One of the simplest examples may be the title compound, 12-hydroxyoctadecanoic acid (12HOA, hereafter), which is an industrial product used as oil solidifier, grease, viscosity adjuster for cosmetics, and so on, for its gel formation ability with oils and organic solvents. The product is obtained by hydrogenation of naturally occurring ricinoleic acid (12-hydroxy-*cis*-9-octadecenoic acid), the main fatty acid of castor oil. The resultant product is optically active, levorotatory (−) with D-configuration[1] (designated D-12HOA), (*R*)-configuration in *R*–*S*. Circular dichroism (CD) bands around 370 nm with opposite signs were obtained for the gels[2,3] and xerogels[4] of D- and L-12HOA ((*S*)-configuration in *R*–*S*) obtained by the Walden inversion of D-12HOA. The CD spectra were attributed to supramolecular helicoidal structures. Recently, vibrational CD spectra with the opposite signs were measured on gels of D- and L-12HOAs.[5] The gel of 12HOA has been also regarded as a promising template for the syntheses of inorganic oxides[6] and polymerization.[7]

On the other hand, racemic modification (DL-12HOA), which is obtained by the oxidation of D-12HOA to keto-acid, followed by hydrogenation,[8] exists as a racemic compound with a slightly lower mp (79.2 °C) than the chiral (82.0 °C); chiral and racemic 12HOAs form a 75 °C mp eutectic mixture.[9] This means that the racemic compound and chiral counterparts are immiscible in the solid state and are distinctly different systems. Different behavior has long been confirmed for chiral and racemic 12HOAs. Morphology of the precipitates[8] and the collapsed monolayers[10,11] is different: i.e., twisted fibrils for D-12HOA and L-12HOA with the definite sense of the twist depending on the molecular chirality, but platelets for DL-12HOA. Different surface pressures in the water–air interface were measured.[10,11] The most striking difference is however, the fact that D- or L-12HOA forms a gel with various organic solvents, from which DL-12HOA can be crystallized.[2,3] For DL-12HOA, X-ray crystal structure analyses were carried out for single crystals obtained from chloroform/hexane[12] and dichloromethane/hexane,[13] revealing two crystal forms, monoclinic and triclinic, respectively. In contrast, no single crystal data are available for D-form, because of its gel-forming ability with organic solvents.

For more than ten years however, reports have been published that a commercial sample of DL-12HOA had the same ability of gel formation as D-12HOA,[14–18] although they showed no evidence of the specimen being racemic.

In order to clarify the contradictory results, we have reinvestigated the behavior of chiral and racemic 12HOAs. It was clearly shown that gels formed separately from D- and L-12HOAs became a solution when they were put in contact, confirming that DL-12HOA does not form a gel. This paper describes the results of powder X-ray diffraction studies and NMR studies in solution and in the solid state. It was clearly

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shown that different behavior of D- and DL-12HOA originates even in the low concentration range of solutions. Difference in gel-forming ability of D- and DL-12HOA is related to the different equilibrium schemes of aggregation process due to the formation of hydrogen bonds in the solutions.

Experimental

Compounds. D-12HOA was purified by the repeated crystallization of the methyl ester of commercially available 12-hydroxystearic acid (Kanto Chemicals, >80%), followed by hydrolysis, as previously described.[8] The melting point of the compound was measured to be 79.8 °C on a DSC-22C (Seiko) and specific optical rotation [α] of benzene solution was measured on a DIP-181 digital polarimeter (JASCO) with an Hg lamp ($\lambda = 365$ nm) and found to be $-0.84 \pm 0.15°$. Purified D-12HOA was also kindly donated by Dr. E. Satou of Kusumoto Chemicals Ltd. DL- and L-12HOAs were synthesized from pure samples of D-12HOA, as previously described.[8] Intermediate steps in the synthesis and final purities were checked by taking ^{1}H and ^{13}C NMR spectra on a Jeol-AL400. Melting points were 76.2 °C for DL-12HOA, and 74.0 °C for L-12HOA. The [α] values measured under the same conditions as for D-12HOA were $0.0 \pm 0.1°$ for DL-12HOA and $0.80 \pm 0.16°$ for L-12HOA. ^{1}H NMR spectra showed that an impurity of L-12HOA was *cis*-9-octadecenoic acid as a reaction by-product, the amount of which was estimated to be 6.5% (Supporting Information). Thus, L-12HOA was not as pure as D-12HOA but sufficiently pure for the present purpose. We also purchased 12HOA from Aldrich; mp 78.9 °C, [α] $-1.0 \pm 0.2°$. The [α] value shows that the specimen from Aldrich is not DL- but D-12HOA. In order to confirm this point, melting points were measured for the 1:1 mixture of the specimen from Aldrich with the purified D-12HOA sample or the DL-12HOA sample synthesized by us. A significantly decreased mp (65.8 °C) was observed for the mixture with DL-12HOA, while an intermediate mp (79.2 °C) was obtained when mixed with D-12HOA. Octadecanoic acid was purchased from Wako Pure Chemicals (99%, mp: 68.8 °C). Benzene-d_6 (99.9% deuteriated) was purchased from Aldrich.

Methods. Powder X-ray diffraction patterns of D- and DL-12HOA were obtained at room temperature at the BL02B2 in the SPring-8. Samples were filled in a 0.7 mmϕ capillary. The wavelengths used were 0.80040 Å for D-12HOA and 0.80163 Å for DL-12HOA. Exposure time was 10 min. Powder X-ray diffraction analysis for D-12HOA was attempted. By using the DASH[19] program package, the most probable cell parameters obtained were $a = 46.61(2)$, $b = 4.753(5)$, $c = 16.952(8)$ Å, $\beta = 91.02(4)°$ in the monoclinic lattice of space group of $P2_1$ (Supporting Information). Unfortunately however, it was not possible to determine the atomic coordinates of four crystallographically independent molecules by simulated annealing.

NMR spectra in benzene-d_6 were measured at 298 K using 10 mm (o.d.) sample tubes on a Jeol EX-400 FT-NMR spectrometer with the resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C. The solvent ^{1}H and ^{13}C signals were used for chemical shift references, since the solute concentration was sufficiently low not to affect the shift in the present experiment. A stock solution of 7 mmol L^{-1} was prepared, from which each solution was prepared by dilution to the desired concentration.

Solid-state ^{13}C CP/MAS spectra were obtained on a Jeol ECA600 spectrometer at the Chemical Analysis Center of Chiba University. The resonance frequency was 150 MHz and 1000 scans were accumulated.

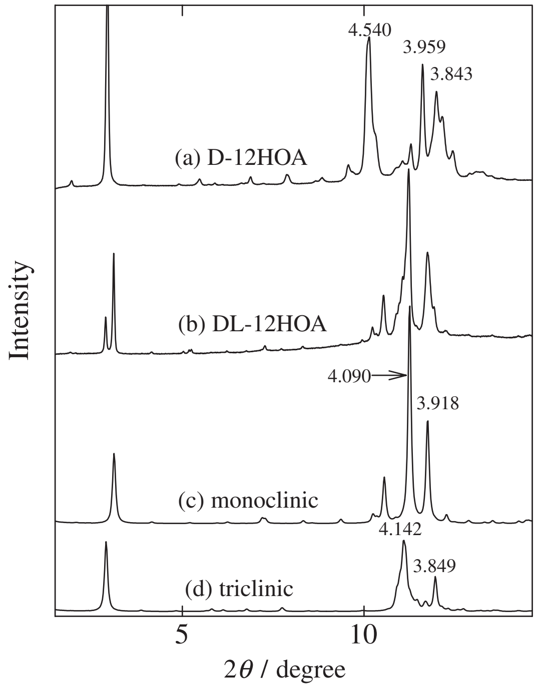

Figure 1. Powder X-ray diffraction patterns of D-12HOA (a) and DL-12HOA (b), and patterns simulated from the monoclinic (c) and triclinic (d) crystal structures of DL-12HOA. Numerical values are *d*-spacings (Å).

Results and Discussion

X-ray Diffraction Studies. Figure 1 shows X-ray diffraction patterns of D-12HOA (a), DL-12HOA (b), and the simulated patterns[20] of the crystal structures of DL-12HOA (monoclinic (c) and triclinic (d)). The patterns of (a) and (b) are quite different; pattern (a) does not coincide with either of the simulated patterns of the two crystal forms of DL-12HOA (c and d), while pattern (b) proved to be a mixture of the two crystal forms.

From the X-ray analysis of DL-12HOA, methylene chains in both crystal forms adopt an orthorhombic $O_\perp$ subcell,[12,13] while a triclinic $T_{//}$ subcell was strongly suggested for methylene chains of D-12HOA from IR spectra and X-ray diffraction patterns.[11] The *d*-value of 4.54 Å for D-12HOA is characteristic of a triclinic subcell and attributable to the (010) spacing of the subcell.[21]

Contact Test. In order to confirm that DL-12HOA has no gel-formation ability, a contact test was performed as follows. Figure 2a shows that both D- and L-12HOAs form a gel with benzene. Here, concentrations were prepared to be 60 mmol L^{-1} for D-12HOA and 80 mmol L^{-1} for L-12HOA to compensate the lower purity of L-12HOA. In Figure 2b, a gel of L-12HOA was first formed at the bottom of a bottle, then a hot solution of D-12HOA was introduced on the L-form gel while cooling, and finally the solution of D-form was quickly cooled to a gel. An interface between the two gels is clearly seen. After 5 min, benzene began to separate out from the gels, as shown in Figure 2c. After 120 min, the gels became a solution with precipitated crystallites in it (Figure 2e). This experiment shows that D- and L-12HOAs together create no gels. It is

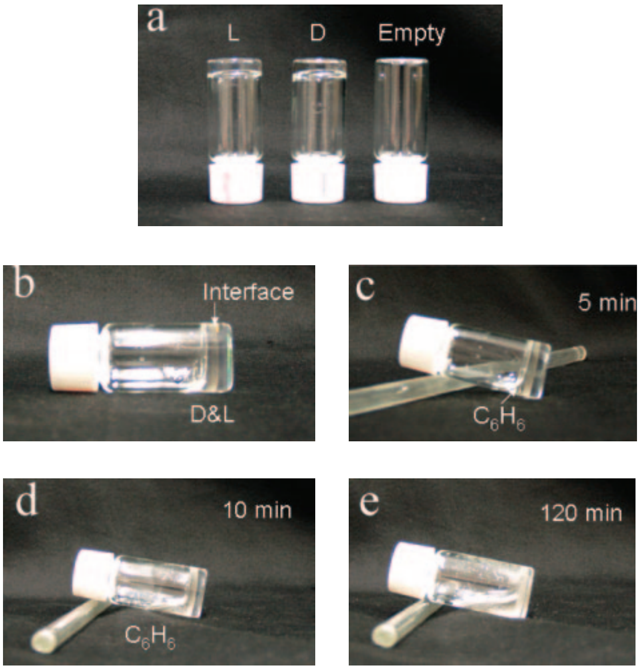

Figure 2. (a) Each L- and D-12HOA forms a stable gel with benzene. (b) A gel of D-12HOA was introduced to a gel of L-12HOA. An interface is clearly seen. (c) After 5 min, benzene began to separate out. (d) After 10 min. (e) After 120 min, the gel became a solution with crystallites.

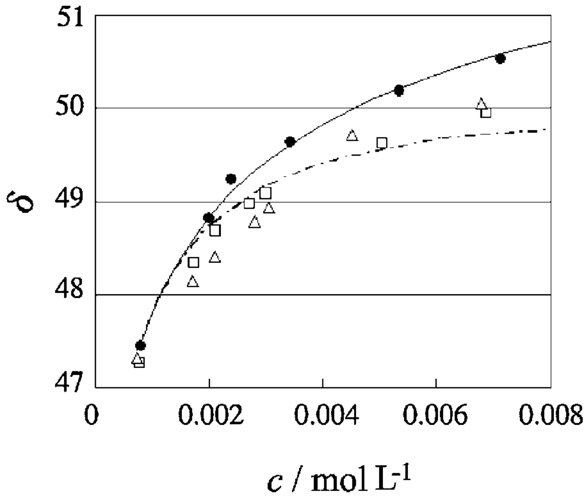

Figure 3. Chemical shifts of octadecanoic acid, D-12HOA, and DL-12HOA in solutions, denoted by ●, □, and △, respectively. Solid and dot-and-dash lines are fitting lines for monomer–dimer equilibrium of octadecanoic acid with $K_{1\text{-}2} = 350$, $\delta_1 = 45.0$, $\delta_2 = 53.7$ and for monomer–dimer–tetramer equilibrium of D-12HOA with $K_{2\text{-}4} = 300$, $\delta_4 = 49$, respectively. The δ values are represented as the differences from the shift of C_6H_6 (128.000).

also shown that D- and L-molecules migrate from each gel to encounter each other to form a solution of DL-12HOA.

NMR Spectroscopy in Solutions. In order to elucidate the molecular aggregation process, NMR measurements were carried out for solutions of benzene-d_6 at 298 K. The concentrations were up to 7 mmol L^{-1}; no generation of gels (for D-12HOA) or crystals (for DL-12HOA) was observed on keeping the 7 mmol L^{-1} solutions for an extended period of time (2 days).

The chemical shifts of carboxy and hydroxy proton should be good indicators for hydrogen-bond formation. The shifts however were not measured since considerable line broadening due to proton exchange with trace amounts of water in the sample solutions was observed. The shifts of the other protons, i.e., the CH protons did not show meaningful concentration dependences.

Carbon-13 NMR spectra were measured for D-12HOA, DL-12HOA, and octadecanoic acid solutions. The measurements for the octadecanoic acid solutions were carried out as a dimer formation model. A low-field shift was observed only for the carboxyl carbons as the concentration increased, as shown in Figure 3. Here, the δ values are represented as the low field shift from C_6H_6. The shifts in the D-12HOA, DL-12HOA, and octadecanoic acid solutions are almost the same in the low concentration range (<1 mmol L^{-1}). This result is ascribed to hydrogen-bond formation in similar extent in the carboxyl groups of all the acids over the concentration range. In the higher concentration range the shifts in the D- and DL-12HOA solutions become smaller than that of the octadecanoic acid solution. Furthermore, slight but definite differences were observed between the D- and DL-12HOA solutions; the shifts for the DL-12HOA solutions are smaller than that of D-12HOA solutions in the concentration range of 1–3 mmol L^{-1}, while the shifts of the former become larger in the higher concentration range (>5 mmol L^{-1}).

The concentration dependence of the shifts is considered as follows. First, we confirm that the low-field shift in the octadecanoic acid solution with the concentration increase is attributed to aggregate formation by hydrogen bond between carboxyl groups. In the case of the octadecanoic acid solutions, only the dimer formation is considered[22–25] since the existence of the higher order aggregates, trimer, tetramer, etc. is negligible. The concentration dependence of the shifts is then analyzed in the following manner. Total concentration, C, and equilibrium constant, $K_{1\text{-}2}$, can be expressed in terms of monomer concentration, [A], and dimer concentration, [A_2], as $C = [A] + 2[A_2]$ and $K_{1\text{-}2} = [A_2]/[A]^2$. Fraction of molecules in monomers, P_1, and in dimers, P_2, are expressed as $P_1 = [A]/C$ and $P_2 = 2[A_2]/C$. Assuming two inherent values of the chemical shifts, δ_1 and δ_2, for the monomer and the dimer, respectively, the chemical shift δ observed is expressed as $\delta = P_1\delta_1 + P_2\delta_2$. With these equations, the parameters of $K_{1\text{-}2}$, δ_1, and δ_2 are obtained by fitting the observed chemical shifts. This monomer–dimer equilibrium model fits very well in the whole concentration range (up to 0.02 mol L^{-1}), giving $K_{1\text{-}2} = 350$, $\delta_1 = 45.0$, $\delta_2 = 53.7$. The equilibrium constant is comparable to those reported for acetic acid in benzene, 370[22] (303 K) and 500 ± 50[23] (301 K), propionic acid in benzene, 390[22] (303 K), butyric acid in benzene, 430[22] (303 K), hexanoic acid in trichloroethylene, 427[24] (298 K), and for benzoic acid in benzene, 390 ± 90[25] (298 K). It is also pointed out that δ_2 is reasonably larger than δ_1, and the shift difference is similar to the value of 5.4–7.4 obtained by density functional calculation for 2-hydroxybenzoic acid.[26]

The low-field shifts in the D- and DL-12HOA solutions are smaller than that of the octadecanoic acid solutions in higher concentration range ($>2\,\text{mmol}\,\text{L}^{-1}$). The results are attributed to higher aggregate formation, e.g. tetramer, hexamer, etc., since the hydrogen-bond linkage between the hydroxy groups in the dimer molecules is observed in the crystalline state of DL-12HOA. To account for the formation of the tetramer, i.e., dimerization of the dimers, the observed concentration dependences of the shifts are analyzed as follows. The equilibria, $A + A \rightleftharpoons A_2$ and $A_2 + A_2 \rightleftharpoons A_4$ are considered, where A_4 is the tetramer. Total concentration, C, and equilibrium constant, $K_{2\text{–}4}$, can be expressed in terms of [A], [A_2], and tetramer concentration, [A_4], as following equations.

$$C = [\text{A}] + 2[\text{A}_2] + 4[\text{A}_4] \tag{1}$$

$$K_{2\text{–}4} = [\text{A}_4]/[\text{A}_2]^2 \tag{2}$$

Fraction of P_4 can be expressed as $P_4 = 4[\text{A}_4]/C$. Assuming three chemical shifts δ_1, δ_2, and δ_4, for monomer, dimer, and tetramer, respectively, chemical shift δ observed can be then expressed as $\delta = P_1\delta_1 + P_2\delta_2 + P_4\delta_4$. With these equations, the parameters, $K_{2\text{–}4}$ and δ_4, were obtained by fitting the observed chemical shifts. Here, the parameters of $K_{1\text{–}2}$, δ_1, and δ_2 were assumed to be the same as those derived for octadecanoic acid, since the δ values of D-, DL-12HOA, and octadecanoic acid approach asymptotically the same value as the concentration becomes low ($<1\,\text{mmol}\,\text{L}^{-1}$).

For D-12HOA, the most probable fitting was obtained, as shown in Figure 3 by dash-and-dot line, when $K_{2\text{–}4} = 300$ and $\delta_4 = 49$. The value of δ_4 is between δ_1 and δ_2. The decrease in δ_4 compared with δ_2 can probably be ascribed to the magnetic anisotropy of the carboxy (or carbonyl) groups in the neighboring dimers as well as a modification of the hydrogen-bond structure on the formation of tetramer, since the high field shift due to the magnetic anisotropy is thought to be up to several ppm at the maximum.[27] The fitting curve agrees well with the experimental values except for the highest concentration range around $7\,\text{mmol}\,\text{L}^{-1}$. The deviation most likely indicates formation of higher aggregates to a significant extent, promoted by the hydrogen bond through the hydroxy groups of 12HOA.

On the other hand, the fitting curve using the δ_1, δ_2, δ_4, $K_{1\text{–}2}$, and $K_{2\text{–}4}$ applied for the D-12HOA solutions did not reproduce the concentration dependence of DL-12HOA solutions; experimental values are significantly smaller than those of the fitting curve in the low concentration range ($<4\,\text{mmol}\,\text{L}^{-1}$), while they become larger than those of the fitting curve in the higher concentration range ($>4\,\text{mmol}\,\text{L}^{-1}$). Any parameter set of δ_4, and $K_{2\text{–}4}$ gave worse fitting, under the constraint condition of the values of δ_1, δ_2, and $K_{1\text{–}2}$ to be the same as those of octadecanoic acid and D-12HOA. These results are ascribed to difference in the extent of higher aggregates formation and/or in the shift change in the formation of the aggregates between the D-12HOA and DL-12HOA solutions.

In the DL-solution, there are possibilities of finding tetramers composed of all D- or L-molecules (D_4 and L_4), three D-molecules and one L-molecule and vice versa (D_3L and DL_3), and two D-molecules and two L-molecules (D_2L_2). The interaction between the hydroxy groups for the D–D (or L–L) pairs and for the D–L pairs should be different. In fact, in both crystal structures, monoclinic and triclinic, D- and L-molecules form a pair connected by the hydrogen bond between the carboxyl groups and the pairs are arranged upside-down, leading to the alternate arrangements of D- and L-molecules. The equilibrium constant for D_2L_2 formation is reasonably assumed to be larger than those for other aggregates. Thus, the difference of the concentration dependence of the low-field shift between the D- and DL-12HOA solutions is attributable mainly to racemic tetramer, D_2L_2.

It is almost impossible to construct a fitting model to account for the concentration dependence of δ in the DL-12HOA solutions in which various species are present in variable concentrations. Thus, considering the situation mentioned above, we attempted to treat the difference between the D- and the DL-12HOA solutions only qualitatively as follows. For smaller experimental values of the DL-12HOA solutions than expected from the monomer–dimer–tetramer equibrium model in the low concentration range, it is interpreted that the ratio of tetramers is larger than in the D-12HOA solutions: dimers are more aggregated to tetramers than in the D-12HOA solutions in the low concentration range. And if more tetramers are produced, the formation of higher aggregates such as hexamer should be more promoted than in the D-12HOA solutions. In order to examine these interpretations, the equilibrium model was modified. First, $K_{2\text{–}4}$ for dimer–tetramer equilibrium was assumed to be larger than that for D-12HOA, while parameters of monomer–dimer equilibrium were fixed to be the same as before, $K_{1\text{–}2} = 350$, $\delta_1 = 45.0$, and $\delta_2 = 53.7$, because the hydroxy group on C12 does not participate in the dimer formation. Second, the formation of hexamer (A_6), $A_4 + A_2 \rightleftharpoons A_6$, was additionally considered in the model, in order to account for the deviation in the higher concentration range. Similar to the monomer–dimer–tetramer equilibrium model, equilibrium constants, $K_{2\text{–}4}$ and $K_{4\text{–}6}$ ($=[\text{A}_6]/([\text{A}_4][\text{A}_2])$), δ_4, and δ_6 (for hexamer) were roughly estimated by fitting the observed chemical shifts. The best fit was obtained when $K_{2\text{–}4} = 1000$, $K_{4\text{–}6} = 1000$, $\delta_4 = 47$, and $\delta_6 = 53$, which is shown by solid line in Figure 4. Here, the result of $K_{2\text{–}4} = K_{4\text{–}6}$ was not postulated but accidental. The curve fits better than the previous one (dotted line) in the low concentration range. Thus, it is concluded that tetramer formation is more favorable for DL-12HOA than for D-12HOA in the low concentration region. In the higher concentration range, although the deviation is still large, the concentration dependence becomes better fitted as a whole. Probably higher aggregates than hexamer should be assumed. However, the new model explains the whole tendency better than the previous one, which justifies our interpretation at least qualitatively.

The results are schematically summarized in Figure 5. The lower value of δ_4, as well as the higher value of $K_{2\text{–}4}$ for DL-12HOA, compared with D-12HOA, is consistent with the assumption that the tetramer formation is more favorable for DL-12HOA than for D-12HOA, showing that the tetramer in DL-12HOA is more firmly organized. On the other hand, the higher value of δ_6 (53 ppm) than δ_4 (47 ppm) for DL-12HOA suggests a geometric rearrangement of the dimeric carboxy moieties on the addition of the third dimer to a tetramer, because of the direction- and distance-dependent shielding effect by magnetic anisotropy of neighboring carbonyl

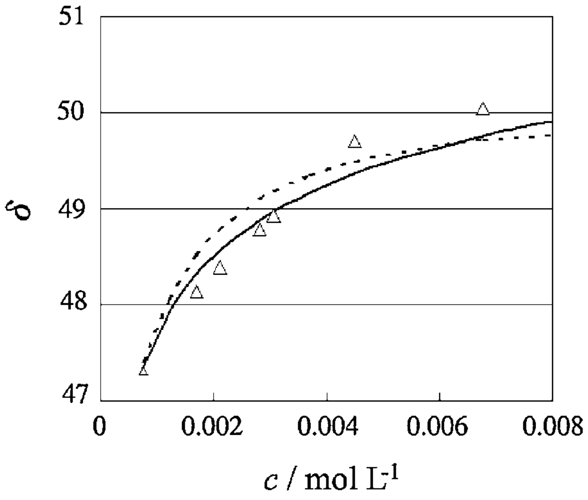

Figure 4. Chemical shifts of DL-12HOA, denoted by △. Solid line is the fitting line of monomer–dimer–tetramer–hexamer equilibrium with $K_{2\text{–}4} = 1000$, $K_{4\text{–}6} = 1000$, $\delta_4 = 47$, and $\delta_6 = 53$. Dotted line is the fitting line of monomer–dimer–tetramer equilibrium shown in Figure 3.

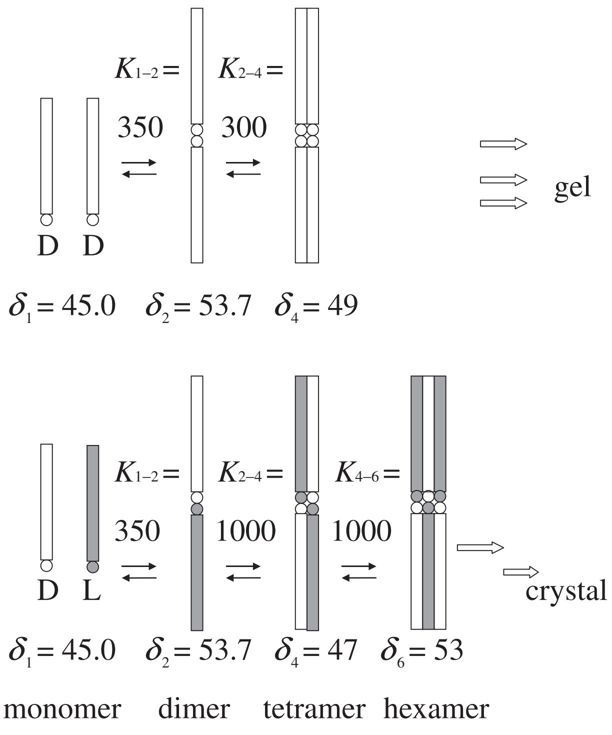

Figure 5. Schematic summary of the NMR results in solutions of D-12HOA (upper) and DL-12HOA (lower). Long rectangles and small circles denote chains and polar head groups, respectively. The molecules in the hexamer do not necessarily align in a line as shown.

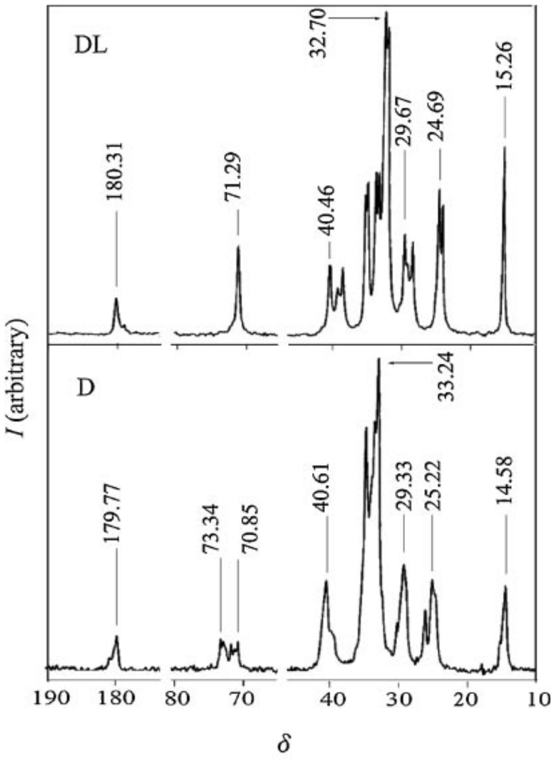

Figure 6. Solid-state NMR spectra for DL-12HOA (upper) and D-12HOA (lower).

groups[27,28] as well as hydrogen bond structure modification. Thus, we conclude that the tetramer and higher aggregates formation is more favorable, and hence the hydrogen bonds between hydroxy groups at C12 are more favorably developed in the DL-12HOA solutions than in the D-12HOA solutions. Unfortunately however, we do not know the crystal structure of D-12HOA, which prevents us from drawing a precise picture accounting for the difference of the hydrogen-bond formation between D- and DL-12HOA. Nevertheless, we found that the difference between the D- and DL-12HOA solutions in the concentration dependence of the low-field shifts, which is assigned to the different extents of higher aggregates formation more favorable in the DL-12HOA solutions than in the D-12HOA solutions. The ratio of monomer, dimer, tetramer, and hexamer is estimated to be 0.2, 0.2, 0.3, and 0.3, respectively, for the DL-12HOA solution, while the ratio of monomer, dimer, and tetramer is estimated to be 0.3, 0.4, and 0.3, respectively, for the D-12HOA solution, both at 7 mmol L^{-1}. In more concentrated solutions of DL-12HOA, it is interpreted that higher aggregates are successively produced, leading to the formation of crystals. In the D-12HOA solutions on the other hand, it is suggested that the size of aggregates remains rather small and the number of the small aggregates such as tetramer increases, which would aggregate rather abruptly upon the solubility limit into a gel.

Solid-State NMR Spectroscopy. In the preceding section, different hydrogen-bond formation was observed even in solutions in the low concentration range. In order to elucidate the difference of the resultant hydrogen bonds in the aggregated states, we measured NMR spectra in the solid state.

As shown in Figure 6, different spectra were observed between D- and DL-12HOA. The peaks were assigned as follows;[29] peaks at $\delta = 15$ to the methyl carbon, peaks in the range of $\delta = 24$–44 to methylene groups, peaks at around $\delta = 70$ to C12 carrying an OH group, and peaks at $\delta = 180$ to the carboxyl C.

D-12HOA shows broader peaks than DL-12HOA, as a whole, corresponding to the broad peaks of the X-ray diffraction pattern. The different profiles in the range of methylene groups are attributable to the different packing schemes of methylene chains, orthorhombic $O_\perp$ subcell[12,13] for DL-12HOA and a triclinic $T_{/\!/}$ subcell for D-12HOA, as mentioned in the section of X-ray diffraction.

The peak of C12 is a singlet for DL-12HOA, although DL-12HOA was a mixture of two crystal forms, showing that the surroundings of C12 are essentially the same in the two crystal forms of DL-12HOA. In both structures, all the hydroxy groups participate in infinite zigzag chains of hydrogen bonds with O–O distances of 2.87 Å for the monoclinic form[12] and 2.764 and 2.751 Å for the triclinic form.[13] On the other hand, D-12HOA shows split peaks at about 71 and 73 ppm with components for each. The former corresponds to the peak of DL-12HOA and the latter is higher than it. It is suggested that there are two kinds of hydrogen bonds; one is similarly strong to DL-12HOA and the other is stronger than that of DL-12HOA. In contrast, the chemical shifts of carboxyl C atoms are only slightly different between D- and DL-12HOAs. It is pointed out that the larger shift of DL-12HOA ($\delta = 180.31$) than D-12HOA ($\delta = 179.77$) is compatible with that in the solution of higher concentration. From these results, it is shown that the aggregation processes in the solutions are closely related to the structures of bulk crystals. Hydrogen bonds in a simple mode are favorably connected one by one into one-dimensional chains, resulting in more ordered arrangements of molecules, i.e., well-defined crystalline states, in DL-12HOA.

Conclusion

A contact test clearly showed that DL-12HOA does not form a gel, while D- and L-12HOAs do. Significantly different behavior was found between D- and DL-12HOAs in the solution states. The difference between D- and DL-12HOA in solutions clearly shows that D- and L-molecules recognize each other and associate even in a very dilute solution of DL-12HOA. The concentration dependence of the low-field shift was analyzed based on multiple equilibrium model. It is concluded that successive development of dimers to tetramers and hexamers is more favorable in the DL-12HOA solutions than in the D-12HOA solutions. Solid-state NMR spectra show two kinds of hydrogen bonds for D-12HOA; one with similar strength to that of DL-12HOA and the other stronger than that of DL-12HOA. In addition, complicated peak profiles of C12 indicate a distribution of the hydrogen-bond geometries. On the other hand, a simple mode of hydrogen bonds are favorably connected one by one into one-dimensional chains, resulting in more ordered arrangements of molecules, i.e., well-defined crystalline states, in DL-12HOA.

Supporting Information

^{1}H NMR spectra showing the purity of L-12HOA and the results of Pawley refinement of powder XRD of D-12HOA. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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