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Comparison of Vibrational Circular Dichroism between the Langmuir–Blodgett Films and Gels of 12-Hydroxyoctadecanoic Acid

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Vibrational circular dichroism spectroscopy is applied to the gels and Langmuir–Blodgett (LB) films of *R*- and *S*-12-HOA deposited on glass substrates (50 X-type layers) in the wavenumber region of 2700–3400 cm^{-1}, revealing that no long sequence of intermolecular hydrogen bonding was formed in the LB films at C12 position in contrast with the gels of the same compounds.

Vibrational circular dichroism (VCD) is an extension of electronic circular dichroism (ECD) into the infrared and near-infrared regions of the spectrum where vibrational transitions occur in the ground electronic state of a molecule.[1–7] One advantage of VCD over ECD is that the simulation of the former spectra consisting of a large number of normal vibrations is possible by use of a commercial program.[8] The conformation of a chiral molecule is determined by comparing the observed and calculated spectra.[1] However, the signal level of VCD is very low, or the ratio of dichroic effect to absorbance ($\Delta A/A$ or g-factor) is in the order of 10^{-6}. This has limited the application of the method to solution samples of stable compounds. Accordingly only few examples have been reported for thin film systems.[9–11]

A chiral fatty acid, *R*- or *S*-12-hydroxyoctadecanoic acid (denoted by *R*- or *S*-12-HOA, respectively), is known to form a gel consisting of fibrils with helical structure.[12–23] One remarkable feature is that gelation takes place exclusively for the enantiomeric forms of the gelator, but not for a racemic mixture.[13–17] The LB films of the same materials were also prepared to investigate the chirality effect on two-dimensional molecular packing.[23] It remained to be clarified, however, what role hydrogen bonds play in the molecular stacking films and how it differs between gels and LB films.

In the present work, the VCD spectra were compared between LB films and gels in the wavenumber range of 2000–4000 cm^{-1}. This region exhibits the peaks characteristic of C–H stretching vibrations in the alkyl chains as well as the O–H stretching vibrations at C12 position. The analyses of these vibrations were expected to give a clue to the connectivity of 12-HOA molecules through hydrogen bonding. As far as we know, this is the first report of the VCD spectra of LB films.

Purified *R*-12-HOA was donated by Kusumoto Ind. Co. (Japan). The purity of the material was investigated chromatographically on a chiral column and stated to be 99% ee. *S*-12-HOA was synthesized according to a reported procedure.[13] Both materials were analyzed by ORD and NMR spectra: $[\alpha]_{365}$ -0.84 ± 0.15 and $+0.80 \pm 0.16$ for *R*- and *S*-12-HOA, respectively.[14]

For preparing a LB film, a chloroform solution of *R*- or *S*-12-HOA (1 mM) was spread onto an aqueous hydrochloric acid solution (0.01 M) at 20 °C. The π–A curve was recorded in the same way as reported in the literature.[23] A floating film was transferred onto a hydrophobic glass plate ($2 \times 2\,\mathrm{cm}^2$) at 15 mN m^{-1} as an X-type film (downward deposition). The plate was made hydrophobic by being soaked in a toluene solution of benzyltrichlorosilane (0.5%) for 5 h. Transfer-ratio was calculated to be 0.70–0.90. VCD spectra were recorded on the films of 50 layers. The preparation of gel samples was described previously.[7,24] Samples were sandwiched by two CaF$_2$ plates equipped with a Teflon spacer.

The VCD and IR spectra were measured using a PRESTO-S-2007 VCD/RAS spectrometer (JASCO, Japan). Absorption signals were detected using a liquid-nitrogen-cooled InSb infrared detector equipped with ZnSe windows. We used glass substrates for depositing LB films so that it was impossible to measure the IR and VCD signals below 2500 cm^{-1}. In the case of gel samples, we reported the VCD spectra in the wavenumber region of 1000–1800 cm^{-1}.[7]

Figure 1 shows the VCD and IR spectra of the LB film of *R*- or *S*-12-HOA in the wavenumber range of 2700–3400 cm^{-1}, respectively. As for the IR spectra, the peaks at 2850 and 2920 cm^{-1} were assigned to the symmetric and asymmetric C–H stretching vibrations of methylene groups, respectively. There was a shoulder observed around 2960 cm^{-1}, which might be assigned to either the C–H stretching vibration of methyl groups or the O–H stretching of a carboxyl group. The broad band with a peak at 3220 cm^{-1} was assigned to the stretching vibrations of O–H groups at C12 positions. As for the VCD spectra, nearly

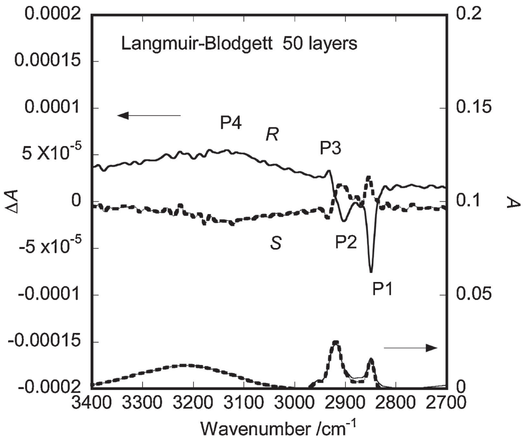


Figure 1. The observed VCD (upper) and IR spectra (lower) of the LB films of *R*- (solid) and *S*-12-HOA (dotted) deposited on glass substrates in the wavenumber ranges of 2700–3400 cm^{-1}, respectively.[24]

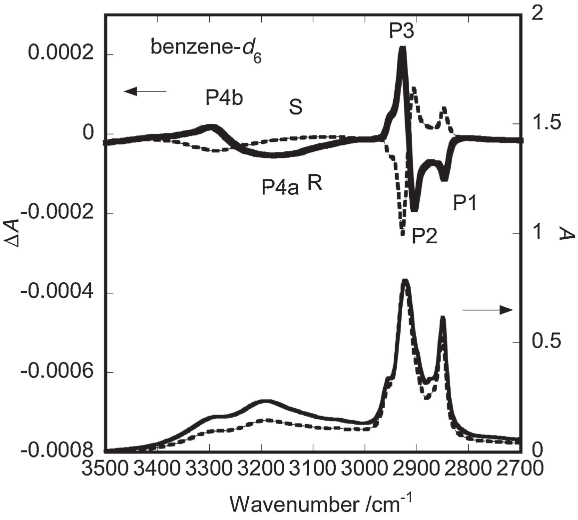
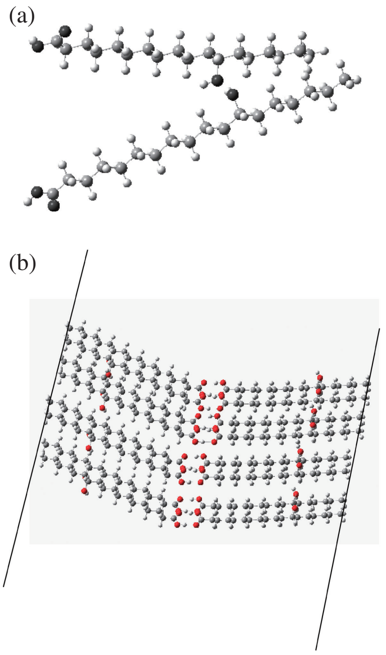


Figure 2. The observed VCD (upper) and IR spectra (lower) of the benzene-d_6 gels of *R*- (solid) and *S*-12-HOA (dotted) in the wavenumber ranges of 2700–3500 cm^{-1}.

mirror-imaged signals were observed between the antipodal films.[24] No change of the signals was observed when the sample plate rotated by 90 degrees, excluding the effect of linear dichroism. The first two peaks corresponding to the symmetric and asymmetric stretching vibrations of C–H bonds in the alkyl chain showed the same sign and denoted by P1 and P2, respectively. The third peak corresponding either to the stretching vibration of O–H bond at the carboxyl group or to the C–H stretching vibrations of methylene groups, denoted by P3, showed the opposite sign to those of P1 and P2. The broad bands corresponding to the stretching vibrations of O–H groups at C12 positions, denoted by P4, showed the same sign as that of P3. The peak position of P3 in the VCD spectra was 3130 cm^{-1}, which displaced by 90 cm^{-1} toward lower wavenumber than that in the IR spectra. The facts might indicate the presence of more than two transitions in this band.

Figure 2 shows the results of similar measurements on the transparent benzene-d_6 gels of *R*- and *S*-12-HOA, in the same wavenumber region. As for the IR spectra, they were nearly the same as for the LB films except for the fact that the broad band due to the stretching vibration of OH bonds consist of two peaks at 3200 and 3300 cm^{-1}. The results suggested that there were two types of hydrogen bonds in the gels. The VCD spectra differed remarkably between the LB films and gels. The peaks were denoted by P1, P2, and P3 in the region of 2700–3000 cm^{-1}. The signs of P1, P2, and P3 were the same as in the LB films, although the relative intensity among these peaks was different. As for the broad peak around 3200 cm^{-1}, the split peaks were denoted by P4a and P4b as indicated in Figure 2. They showed opposite signs, corresponding to the two peaks in the IR spectra.

In order to simulate the VCD spectra of the gels, IR and VCD spectra were calculated on the basis of magnetic field perturbation (MFP) theory.[8] The molecules were assumed to form a dimer in gels. In a previous paper on gel samples, we calculated the VCD spectra for several dimer models.[7] As a result, the best agreement between the observed and calculated spectra was attained for the bend dimer model in which two monomers were bridged by the hydrogen bonding at carboxylic groups in a bent conformation.[24] In the LB films, we supposed that the formation of such a dimer would be difficult because the molecules oriented in the same direction for the X-type deposition, unless some flipped their orientation within a layer. Accordingly the following dimer model was proposed (Scheme 1a), in which two molecules were connected at the O–H groups at C12 positions. The structure was optimized for this type of dimer. Figure 3 shows the calculated spectrum under this conformation.



Scheme 1. (a) The optimized structure of a pair of *R*-12-HOA molecules connected by the hydrogen bonding at OH groups for a model of LB films. (b) The possible structure of a gel state.

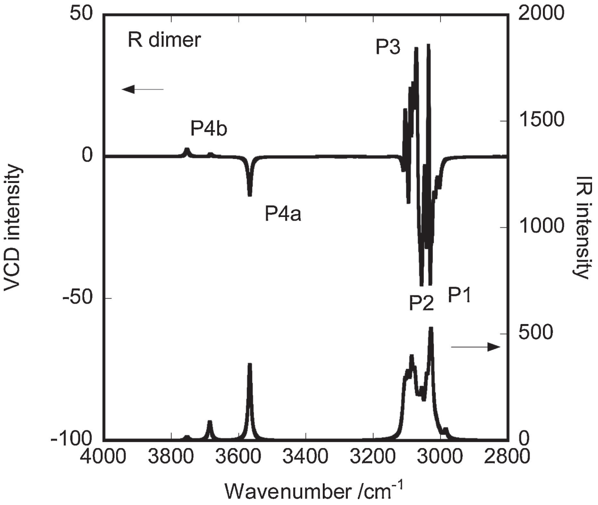


Figure 3. The calculated VCD (upper) and IR spectra (lower) of an *R*-12-HOA dimer in the wavenumber range is 2800–4000 cm^{-1}. The dimer was assumed to form a hydrogen bond at the C12 positions as shown in Scheme 1a.

According to the calculation, the bands due to the C–H stretching vibrations in the region of 3000–3100 cm^{-1} well reproduced the observed spectra as indicated by P1, P2, and P3. Moreover, the O–H stretches at C12 positions were predicted to give two peaks at 3570 and 3680 cm^{-1} with opposite signs as indicated by P4a and P4b in the observed spectra (Figure 2), respectively. According to this dimer model, the split of the broad band around 3200 cm^{-1} reflected the formation of intermolecular hydrogen bonding. The calculation confirmed that both the IR and VCD peaks due to the OH groups showed very low intensity for a monomer,[24] while they gave high intensity when they formed an intermolecular hydrogen bond. Accordingly, we have proposed the possible gel states model as shown in Scheme 1b.

The absence of splitting of the band observed for the LB films might imply that no regular chain of the intermolecular hydrogen bonds was formed in the LB films. Since the molecules do not orient randomly in the LB films, it might be difficult to form the chain of hydrogen bonding extending over a large number of molecules.

The present paper compares the VCD spectra of the LB films of 12-HOA and gels. As a result, the difference in the hydrogen bonding was revealed between these samples, which were not deduced from the IR spectra alone. The results demonstrated the potentiality of VCD spectroscopy for structural studies of gel and film systems.

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