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Raman Spectroscopic Study of Alternate Langmuir-Blodgett Films with Pyroelectric Efficiency

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Non-resonance Raman spectra of an alternate Langmuir-Blodgett (LB) film of 5-(p-dodecyloxyphenyl) pyrazine-2-carboxylic acid (DOPPC) and deuterated stearic acid (SA-d₃₅) was recorded at various temperatures. The same measurements were also performed for the alternate LB film of their Ba salts. From the intensity ratio of the antisymmetric to symmetric CH₂ stretching bands of DOPPC and the bandwidth of the symmetric CD₂ stretching band of SA-d₃₅, it was found that upon heating the film the hydrocarbon chains of both DOPPC and SA-d₃₅ start to change from the ordered state to the disordered state at ca. 35 and 45°C in acid and Ba salt films, respectively.

KEY WORDS: Non-resonance Raman Spectra / Alternate Langmuir-Blodgett Films /
Pyroelectric LB Films / CCD Detector

INTRODUCTION

In recent years, Langmuir-Blodgett (LB) films have attracted much interest as highly organized assembly with new functions. In particular, the alternate or hetero LB film which is constructed by the alternate deposition of two different amphiphiles has an organic superlattice structure with noncentrosymmetry, and is expected to show pyroelectric, piezoelectric, and non-linear optical properties.¹⁾ In a previous paper,²⁾ by combining Fourier transform infrared (FT-IR) transmission and reflection absorption (RA) techniques,³⁾ we have quantitatively evaluated the molecular orientation in alternate LB films of 5-(p-dodecyloxyphenyl) pyrazine-2-carboxylic acid (DOPPC or simply P) and deuterated stearic acid (SA-d₃₅ or simply S) and of their Ba salts, DOPPC-Ba and SA-d₃₅-Ba, at room temperatures. Further, we have extended the orientation evaluation of the alternate LB film to elevated temperatures, and compared it with the pyroelectric properties.⁴⁾ Therein, we have found that the thermally stimulated current due to depolarization was initiated by the

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conformational disorder of the hydrocarbon chain. On the other hand, it has been shown that the order-disorder transition of the hydrocarbon chain in LB films of the monolayer level can be monitored by examining the bandwidth and intensities of the CH stretching bands in Raman spectra recorded with the charge-coupled device (CCD) detector.⁵⁻⁸⁾ In the present paper, therefore, we have recorded Raman spectra of the alternate LB film of DOPPC and SA-d₃₅ at various elevated temperatures, and examined the order-disorder properties of the hydrocarbon chain, in order to confirm the infrared results.⁴⁾

EXPERIMENTAL

The alternate LB film of the structure S(PS)₂₁, with 1-monolayer of S and 21-layers of a unit alternate bilayer, PS, was fabricated on a quartz prism by the procedure described previously.^{2,4)} The alternate LB film of the corresponding Ba salts with the structure S(PS)₂₁-Ba was also made in a previous manner.^{2,4)}

Non-resonance Raman spectra of the alternate LB films were recorded by a total reflection method of the excitation beam, as shown in Fig. 1.^{7,8)} Although, we tried to use the exci-

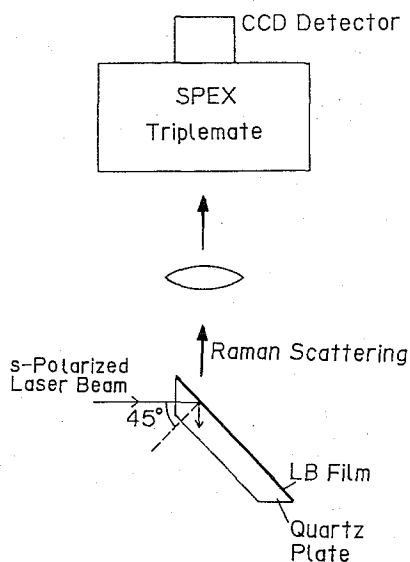


Fig. 1. Total Reflection method for Raman measurements of LB films.

tation light at 488.0 nm or 514.5 nm of the Ar⁺ laser, Raman measurements were impossible due to high fluorescence levels of DOPPC. Thus, we used the 647.1-nm line of a Coherent Model Innova-90 Kr⁺ laser as the excitation source. The interference filter was used to remove the spontaneous emission lines. The output power of 450 mW was reduced to 250 mW at the sample position in our experimental set-up. The s-polarized beam of 647.1 nm was incident on the film surface at the angle of 45° and was totally reflected. The Raman scattering

was collected in the direction normal to the excitation beam and was introduced to a Spex Triplemate 1877 monochromator equipped with a Photometrics Model PM512 CCD detector with $20 \mu\text{m}$ square pixels of 512 columns by 512 rows. The monochromator has the polarization ($I_{//}/I_{\perp}$) of 1.9 and 3.0 in the CH and CD stretching regions, respectively. The CCD detector was operated at -125°C by a Photometrics Series 200 cryogenic camera system which consists of a Model CH210 camera head, CE200 electronic unit, and CC200 controller. Read-out noise was reduced by binning ca. 20 columns along the direction perpendicular to the spectral image. The system gain was 15.9 electrons per ADU. The measurement times were 60 min (CD stretching region of $\text{S}(\text{PS})_{21}\text{-Ba}$), 75 min (CH stretching region of $\text{S}(\text{PS})_{21}\text{-Ba}$ and CD stretching region of $\text{S}(\text{PS})_{21}$), and 120 min (CH stretching region of $\text{S}(\text{PS})_{21}$). The slit width of 200 nm used in this experiment corresponds to the optical resolution of about 5 cm^{-1} for a holographic grating of 1200 grooves/mm. An NEC Model PC9801-VX computer was connected to the CC200 camera controller through a GPIB interface, and spectral data obtained were processed and plotted by a Seki CCD software. Temperature of the sample was changed from 0 to 120°C and with the accuracy of $\pm 1^{\circ}\text{C}$ by a Neslab Model RTE-4 refrigerated bath circulating system ($0\text{-}80^{\circ}\text{C}$) or by a sheath heater ($80\text{-}120^{\circ}\text{C}$).⁴⁾

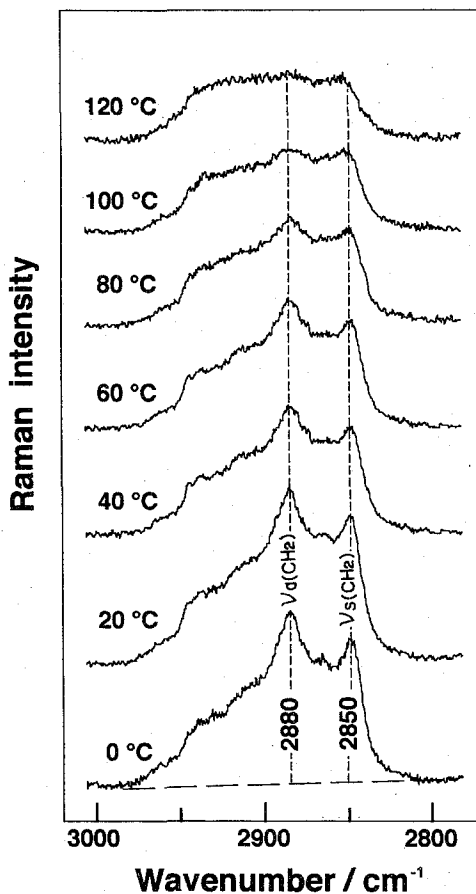


Fig. 2. Raman spectra in the CH stretching region of DOPPC-Ba in $\text{S}(\text{PS})_{21}\text{-Ba}$ film at various temperatures.

RESULTS AND DISCUSSION

Figure 2 shows the Raman spectra of the CH stretching region of DOPPC-Ba in the S(PS)₂₁-Ba film, recorded at various temperatures. The CH stretching region of the long hydrocarbon chain compound exhibits a complex feature due to the presence of Fermi resonance between the CH stretching modes and overtones of the CH₂ scissoring modes.⁹ At 0 °C, there are two strong peaks at ca. 2880 and 2850 cm⁻¹ which are assigned to the antisymmetric and symmetric CH₂ stretching vibrations, respectively, of the dodecyl chain of DOPPC-Ba. Gabor and Peticolas¹⁰ have shown that the intensity ratio $I(2880)/I(2850)$ is a sensitive measure of the order or regularity of the hydrocarbon chain, although it is also affected by the lateral packing order. They reported that the intensity ratio of hexadecane decreases from 1.5 to 0.7 when the hydrocarbon chain changes from the vibrationally decoupled (isolated) all-trans structure to the melted state.¹⁰ Therefore, the intensity ratio $I(2880)/I(2850)$ in Fig. 2 is plotted in Fig. 3, together with the results for DOPPC in the S(PS)₂₁ film as a function of temperature. The ratios are ca. 1.2 for both DOPPC and DOPPC-Ba in the S(PS)₂₁ and S(PS)₂₁-Ba films, respectively, at low temperatures. However, it starts to decrease at ca. 35 °C for DOPPC and at 45 °C for DOPPC-Ba. These temperatures are in good agreement with those of the pyroelectric current minima and the starting points of the increase in the chain tilting angle, reported previously.⁴ Since the measurement conditions are different between Ref. 9 (polycrystalline powder sample, normal scattering) and the present paper (oriented film, total reflection), the direct comparison of the intensity ratios is not possible. However, the results in Fig. 3 clearly indicate that the chain disorder occurs at elevated temperatures above 35 or 45 °C in S(PS)₂₁ and S(PS)₂₁-Ba films, respectively.

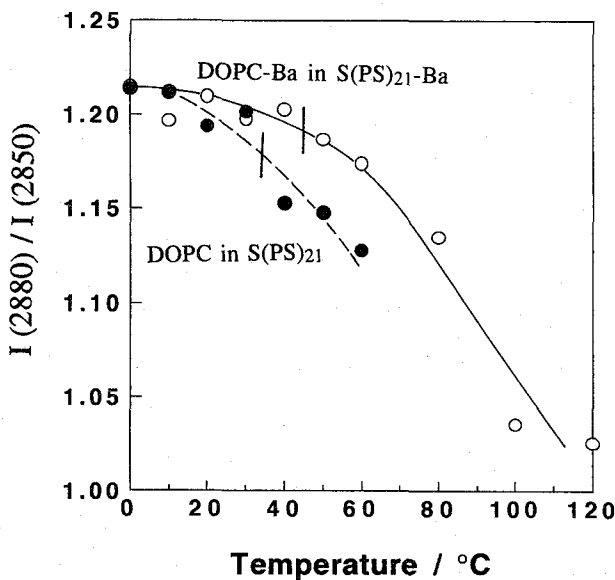


Fig. 3. $I(2880)/I(2850)$ of DOPPC and DOPPC-Ba in S(PS)₂₁ and S(PS)₂₁-Ba films, respectively, as a function of temperature.

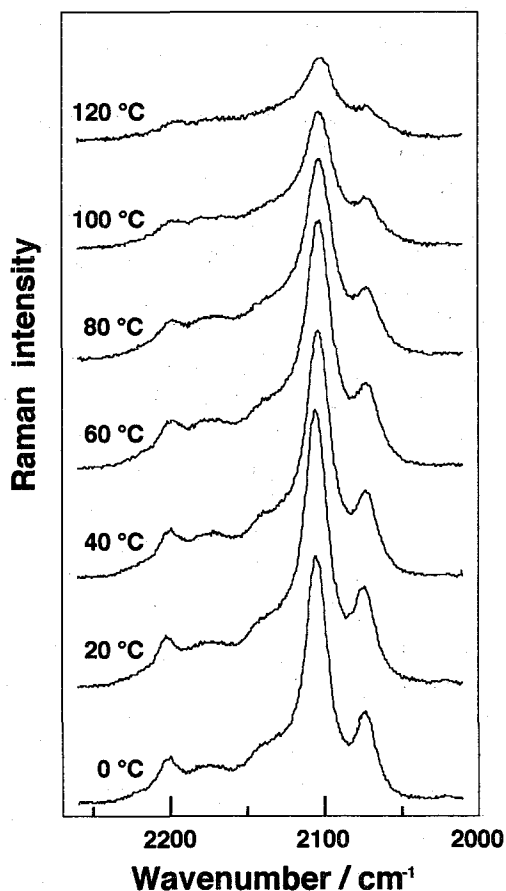


Fig. 4. Raman spectra in the CD stretching region of SA-d₃₅-Ba in S(PS)₂₁-Ba film at various temperatures.

Figure 4 shows the Raman spectra of the CD stretching region of SA-d₃₅ in the S(PS)₂₁-Ba film, recorded at various temperatures. The intense band at 2102 cm⁻¹ at 0 °C has been assigned to the symmetric CD₂ stretching vibration, and the weak band at 2200 cm⁻¹ to the antisymmetric CD₂ stretching vibration.^{7,10-13)} The band at 2075 cm⁻¹ could be assigned partly to one component of a Fermi resonance pair of the CD₂ symmetric stretching vibration (another component is a 2102 cm⁻¹ band) and partly to the symmetric CD₃ stretching vibrations.¹⁰⁻¹²⁾ With increasing temperature, bands become broadened and their peak intensities decrease. The bandwidth of the 2102-cm⁻¹ band is known to be sensitive to the gauche/trans ratio or the chain order and insensitive to the interchain coupling.^{7,13)} Therefore, we plotted the bandwidth (FWHM) of the CD₂ stretching band in Fig. 4 with a base-line drawn from 2240 to 2040 cm⁻¹ as a function of temperature in Fig. 5, together with the results of SA-d₃₅ in S(PS)₂₁. At low temperatures, the bandwidth changes slightly with temperature in both acid and Ba salt films, but they start to increase enormously at ca. 35 and 45 °C, respectively, reflecting the increase in the chain disorder and in the molecular rotational motion.

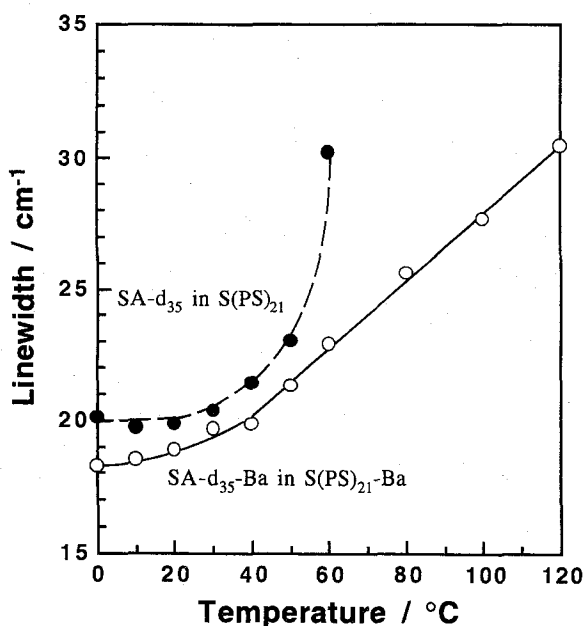


Fig. 5. Halfbandwidths (FWHM) of the 2102 cm^{-1} bands of SA-d₃₅ and SA-d₃₅-Ba in S(PS)₂₁ and S(PS)₂₁-Ba films, respectively, as a function of temperature.

In conclusion, all of these results indicate that the chain disorder increases above the temperature where the pyroelectric current becomes minimal.⁴⁾ Thus, the present Raman spectroscopic measurements confirm the previous statement⁴⁾ that the rapid increase in the positive current observed for the alternating S(PS)₂₁ and S(PS)₂₁-Ba films at higher temperatures above 40–50 °C is due to the depolarization by the increase in the conformational disorder and thermal motion of the hydrocarbon chains.

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