

Raman spectra of Langmuir–Blodgett and Langmuir–Schaefer films of polydiacetylene prepared from 10,12-pentacosadiynoic acid

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Abstract

Blue polydiacetylene films were prepared from the Langmuir–Schaefer (LS) and Langmuir–Blodgett (LB) films of the cadmium salt of 10,12-pentacosadiynoic acid, $\text{CH}_3(\text{CH}_2)_{11}\text{—C}\equiv\text{C—C}\equiv\text{C—}(\text{CH}_2)_8\text{COOH}$, and the $\text{C}\equiv\text{C}$ stretching modes of the Raman spectra of the LS and LB films were observed at 2068 and 2079 cm^{-1} , respectively. These wavenumbers appeared to be sensitive to the packing of polymer chains. Most of the progression bands observed in the range of 1332–1182 cm^{-1} have been assigned to the CH_2 wagging modes of the all-*trans* structure of the $(\text{CH}_2)_{11}\text{CH}_3$ group.

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1. Introduction

Polydiacetylene derivatives are π -conjugated polymers with various side groups (R_1 and R_2 in Fig. 1) and available in single crystals, evaporated thin-films, and LB films. Among numerous conjugated polymers, polydiacetylene has unique properties [1]. Single crystals of polydiacetylene are formed from single crystals of monomers by topochemical polymerization [2]. A drastic color change (so-called ‘blue’ and ‘red’ forms) induced by thermal treatment, light irradiation, etc. has been reported [3,4]. A greenish LB film has also been found [5]. Polydiacetylene single crystals are found to have hole mobilities of 1–10 $\text{cm}^2/\text{V s}$ by the time-of-flight method [6], and their thin-films are used as p-type semiconductors of organic thin-film transistors [7–12]. Their highest field-effect hole mobility, reported to be as high as 0.8 $\text{cm}^2/\text{V s}$ [11], promises wide applications as organic semiconductors of thin-film transistors.

It is thus important to explore the properties of polydiacetylene thin-films, such as π -conjugation, three-dimensional ordering and morphology, to achieve higher carrier

mobility. It has been demonstrated that Raman spectroscopy is useful for characterization of the CC bonds of the main chains [13]. For instance, the blue and red phases exhibit characteristic frequencies of the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ bands [14], and the spectra of self-assembled monolayers [15] and LB films [16] have also been reported. The conformations of alkyl side chains play important roles in the structures and properties of polydiacetylenes. However, they have not been clarified yet. The conformations of *n*-alkanes and related compounds have been investigated mainly by infrared spectroscopy. It is difficult to use infrared spectroscopy for studies of devices consisting of glass, organic compounds, metals, and inorganic insulators. On the other hand, Raman spectroscopy can be used for such studies.

In this Letter, we have prepared thin-films of 10,12-pentacosadiynoic acid cadmium salt by the methods of vertical dipping (for LB) and horizontal lifting (for LS). These films have been photopolymerized by a high-pressure Hg lamp to form blue films of polydiacetylenes. We have studied the molecular structures of these blue LB and LS films by Raman spectroscopy. The observed difference in the wavenumbers of the $\text{C}\equiv\text{C}$ stretching modes for these blue films has provided key information on the conformations of the alkyl side chains.

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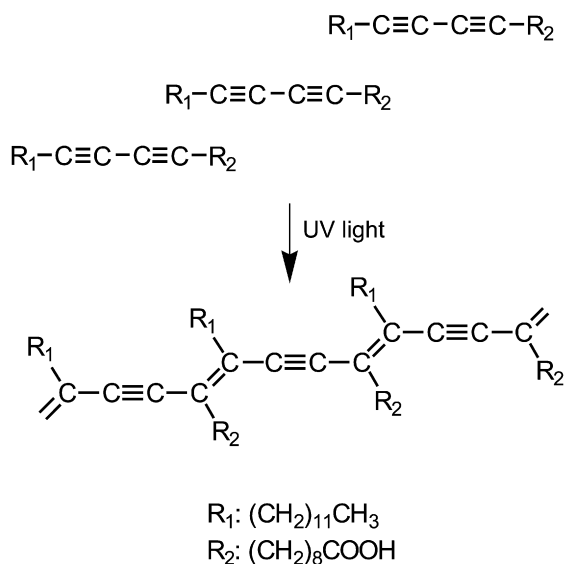


Fig. 1. Structure and photopolymerization process of 10,12-pentacosadiynoic acid.

2. Experimental

10,12-Pentacosadiynoic acid (Tokyo Kasei) was dissolved in chloroform and filtered to remove polymerized solids. LB films were prepared by using a KSV 2000 Langmuir trough with a Wilhelmy balance at room temperature. Water purified in a Millipore Milli-Q SP system (electrical conductivity, $18.3 \text{ M}\Omega \text{ cm}^{-1}$) was used as a subphase. An aqueous solution of CdCl_2 was added to the trough water to a final concentration of $2.5 \times 10^{-4} \text{ mol/L}$. The pH of the solution was adjusted at 6.8 using NaHCO_3 . Monolayers of arachidic acid (Sigma–Aldrich) or 10,12-pentacosadiynoic acid were formed on a trough of water by dropwise addition of chloroform and cyclohexane solutions (1 mg/mL), respectively.

After complete evaporation of the solvent, the molecules were symmetrically compressed by two barriers. The monolayer of the cadmium salt of arachidic acid was first transferred to a quartz substrate three times and used as a spacer. The substrate was washed with a 1:1 mixture of concentrated sulfuric acid and a water solution of hydrogen peroxide (30%). After the deposition of the spacer, ten layers of cadmium 10,12-pentacosadiynoate were deposited at 23 mN/m by the vertical dipping method (for LB) and the horizontal lifting method (for LS) [17]. The LB film of one side was removed. Photopolymerization was performed by exposing the films to UV light from a 450-W high-pressure mercury lamp (Ushio UM-452) with an optical filter (Sigma Koki UTVAF-33U) at a distance of 40 cm. Visible absorption spectra were recorded on a JASCO V-570 spectrophotometer. Micro-Raman spectra were measured on a Raman microprobe (RENISHAW inVia) with excitation at 633 or 532 nm in the back scattering configuration.

3. Results and discussion

3.1. Visible absorption spectra

Figs. 2a and b show the blue polydiacetylene films prepared from the LS and LB films of the cadmium salts of 10,12-pentacosadiynoic acid. These absorptions are attributable to the 1B_u excitons [4]. The LS film exhibits an absorption peak at 636 nm and its vibronic side peak at 584 nm. This is quite similar to the visible absorption spectrum of the blue LS film prepared from metal-free 10,12-pentacosadiynoic acid [5]. On the other hand, the absorption spectrum of the LB film consists of the main peak at 634 nm and its vibronic side peak at 589 nm. This is consistent with the spectrum of the blue LB film reported by Fujimori et al. [5]. The relative intensity of the vibronic peak of the LB film is much stronger than that of the LS film. Probably, the relative intensity of the vibronic peak reflects the solid-state structure of the polydiacetylene film. The blue thin-films of polydiacetylene, prepared by photopolymerization of the evaporated film of 10,12-pentacosadiynoic acid [4,11], were reported to show spectra similar to those reported in the present study.

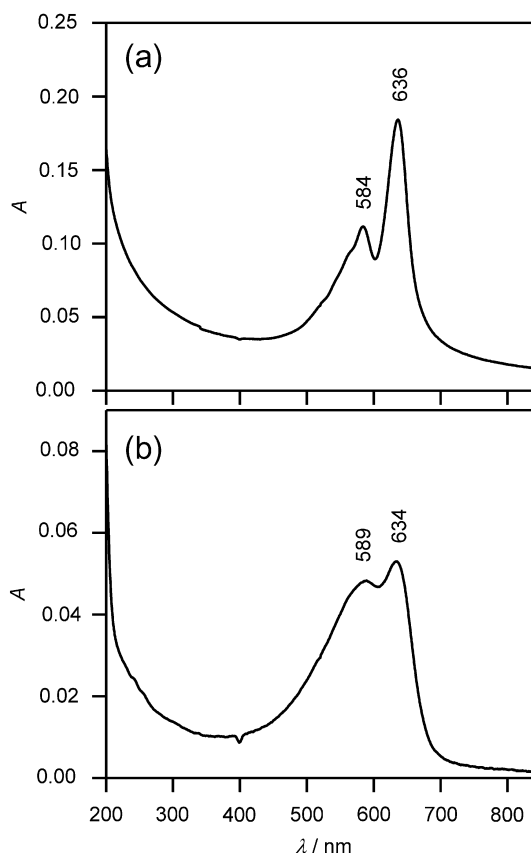


Fig. 2. Visible absorption spectra of the blue (a) LS and (b) LB polydiacetylene films (10 layers deposited at 23 mN/m and room temperature).

3.2. Raman spectra

Figs. 3a and b show the resonance Raman spectra of the blue LS and LB films. The excitation wavelength was 633 nm, which is located within the electronic absorption bands of these films. The bands observed at 2068 and 1448 cm^{-1} of the blue LS film are undoubtedly assignable to the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ stretching modes of the polymer backbone, respectively [14–16]. The bands observed at 2079 and 1448 cm^{-1} of the blue LB film are also assignable to the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ stretching modes, respectively. The 1083- cm^{-1} band of the LS film and the 1084 cm^{-1} band of the LB film have been tentatively assigned to the mixture of the $\text{C}-\text{C}$ stretching modes of the polymer backbone and alkyl side chains, because the blue film of polydiacetylene having the $-(\text{CH}_2)_{15}\text{CH}_3$ groups gives rise to the 1097- cm^{-1} Raman band assignable to the CC stretching mode [18]. The 695- cm^{-1} band of the LS film and the 693- cm^{-1} band of the LB film have been tentatively attributed to the CCC deformation modes associated with the polymer backbone [19]. The $\text{C}\equiv\text{C}$ stretching modes give different wavenumbers for the LS and LB films, whereas the other bands give similar wavenumbers. The wavenumber of the $\text{C}\equiv\text{C}$ stretching mode is expected to be more sensitive to the packing of the polymer chains.

In the Raman spectra of the LS and LB films, distinct progression bands were observed in the region of 1350–1180 cm^{-1} , as shown in Figs. 4a and b. The CH_2 wagging and CH_2 twisting vibrations are expected to appear in this range [20–25]. These bands have been assigned in this study to the CH_2 wagging modes of the all-*trans* alkyl chains, as discussed below. According to a simple coupled-oscillator theory, each vibration of an alkane can be classified by

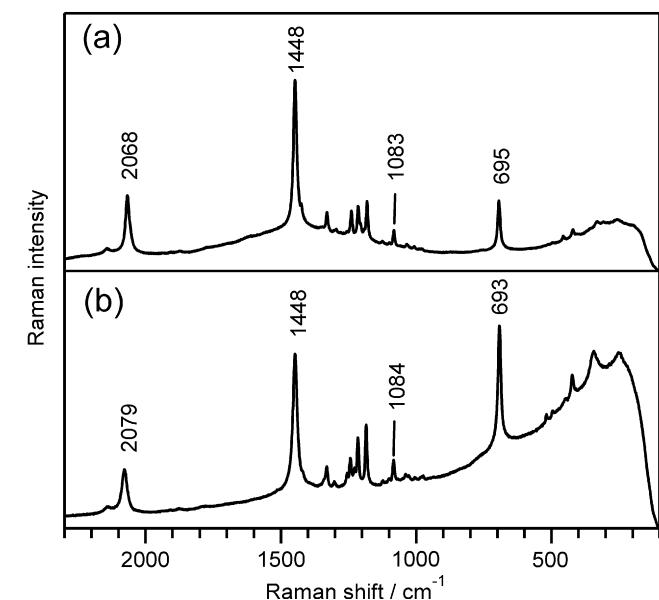


Fig. 3. Raman spectra of the blue (a) LS and (b) LB polydiacetylene films (10 layers deposited at 23 mN/m and room temperature). The excitation wavelength was 633 nm.

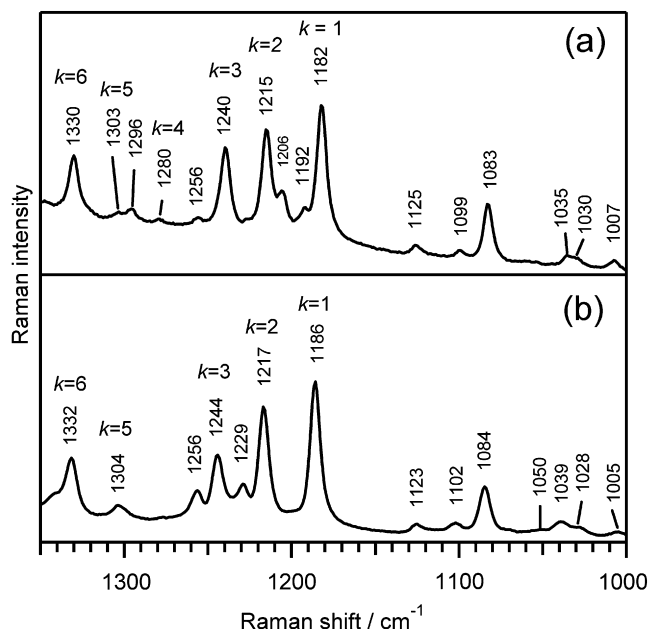


Fig. 4. Raman spectra of the blue (a) LS and (b) LB polydiacetylene films (10 layers deposited at 23 mN/m and room temperature). The excitation wavelength was 633 nm.

the phase difference ϕ between adjacent methylene groups as

$$\phi = \frac{k}{N+1} \quad (k = 1, 2, \dots, N), \quad (1)$$

where N is the number of methylene groups [22–25]. The wavenumbers of the CH_2 wagging vibrations for alkanes ($\text{C}_n\text{H}_{2n+2}$, $n = 20\text{--}30$) in the literature are plotted against the phase differences as dots in Fig. 5. The 1182-, 1215-, 1240-, 1280-, 1303-, and 1330- cm^{-1} bands of the LS film have been assigned to the CH_2 wagging modes with $k = 1, 2, 3, 4, 5,$ and 6 of the $(\text{CH}_2)_{11}\text{CH}_3$ group, respec-

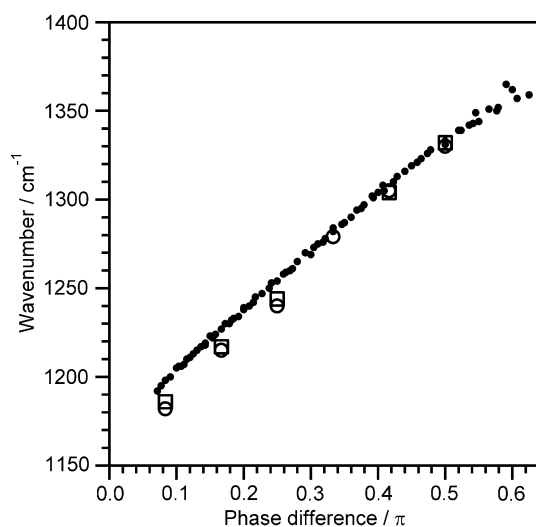


Fig. 5. Plots of wavenumbers versus phase differences for CH_2 wagging vibrations. Dots represent the data of n -alkanes ($\text{C}_n\text{H}_{2n+2}$, $n = 20\text{--}30$) [20]. Open circles and squares are data from the LS and LB films, respectively.

tively. These wavenumbers are plotted as open circles in Fig. 5 on the assumption that the alkyl group takes the all-*trans* conformation ($N = 11$). These data agree well with those of *n*-alkanes. This indicates that the alkyl side group takes the all-*trans* structure. The origins of the other bands observed at 1192, 1206, 1256, and 1296 cm^{-1} are yet unknown, but they are likely to be attributed to the vibrations of the other side group of $(\text{CH}_2)_8\text{COO}^-$. The 1186-, 1217-, 1244-, 1304-, and 1332- cm^{-1} bands of the LB film have been assigned to the $k = 1, 2, 3, 5,$ and 6 modes of the CH_2 wagging of the $(\text{CH}_2)_{11}\text{CH}_3$ group, respectively. These wavenumbers are plotted as open squares in Fig. 5 for $N = 11$. These data also agree well with those of *n*-alkanes. This indicates that the alkyl side group takes the all-*trans* structure. The other bands observed at 1229 and 1256 cm^{-1} that are left unassigned are likely to be attributed to the vibrations of the $(\text{CH}_2)_8\text{COO}^-$ group.

The vibrational progression bands due to the CH_2 wagging mode have been observed in the infrared spectra of *n*-alkanes [20–22], but not in the Raman spectra. In conjugated compounds such as polyacetylene, the vibrational modes that modulate the lengths of the $\text{C}=\text{C}$ and $\text{C}-\text{C}$ bonds (i.e. bond alternation) can gain strong Raman intensities [26]. In polydiacetylene, the vibrational modes that modulate the lengths of the $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, and $\text{C}-\text{C}$ bonds have strong Raman intensities. These modes due to the polymer backbone may be mixed with the $\text{C}-\text{C}$ stretching modes of the alkyl side chain. In the all-*trans* structure of the alkyl side chain, the $\text{C}-\text{C}$ stretching modes can be mixed with the CH_2 wagging modes but not with the CH_2 twisting modes, because the $\text{C}-\text{C}$ stretching and CH_2 wagging modes are symmetric with respect to the plane containing the polymer backbone whereas the CH_2 twisting modes are antisymmetric. Thus, the CH_2 wagging modes of the alkyl side chain are expected to have strong Raman intensities.

Lippert and Peticolas [27] have studied the Raman spectra in the region 1140–1000 cm^{-1} of solid and liquid *n*-alkanes and demonstrated that Raman spectroscopy provides a sensitive probe for analyzing the structures of the alkyl chains. The Raman spectra of all-*trans* structures of *n*-alkanes show two strong bands around 1130 and 1060 cm^{-1} , which are assigned to the $\text{C}-\text{C}$ stretching modes. The Raman spectra of liquid *n*-alkanes in this region is characterized by a broad, intense band at 1090 cm^{-1} , in addition to much weaker bands around 1130 and 1065 cm^{-1} . This 1090- cm^{-1} band is assigned to the $\text{C}-\text{C}$ stretching modes of the structures containing *gauche* conformations. These three bands are used as markers of the structural changes of alkyl chains. On the other hand, the 1125-, 1099-, and 1083- cm^{-1} bands are observed for the blue polydiacetylene LS film, in contrast to the 1123-, 1102-, and 1084- cm^{-1} bands for the LB film, as shown in Fig. 4. These spectral features are quite different from those of *n*-alkanes, because the coupling between the $\text{C}-\text{C}$ stretching modes due to alkyl chains and skeletal vibrations due to the polymer backbone is significant.

4. Conclusions

The Raman spectra of the blue polydiacetylene films prepared from the LS and the LB films of the cadmium salts of 10,12-pentacosadiynoic acid [$\text{CH}_3(\text{CH}_2)_{11}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8\text{COOH}$] have been measured. The 2068-, 1448-, and 1083- cm^{-1} bands of the LS film have been assigned to the $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, and $\text{C}-\text{C}$ stretching modes, respectively, whereas the 2079-, 1448-, and 1084- cm^{-1} bands of the LB film to the $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, and $\text{C}-\text{C}$ stretching modes, respectively. Only the $\text{C}\equiv\text{C}$ stretching modes show significant differences in wavenumbers. This can be explained by the dependence of the $\text{C}\equiv\text{C}$ stretching wavenumbers on the packing of polydiacetylene chains. Most of the progression bands observed in the range between 1332 and 1182 cm^{-1} have been classified by the phase difference between the CH_2 wagging motions of adjacent methylene groups. These features suggest that the $(\text{CH}_2)_{11}\text{CH}_3$ group takes the all-*trans* structure for the LS and LB polydiacetylene films. Thus Raman spectroscopy provides a powerful tool for studies of the conformations of alkyl side chains as well as the molecular structures of polymer backbones, which are closely related to the performance of polymer thin-film transistors.

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