Reversible Thermochromic Change of Molecular Architecture for a Diacetylene Derivative 10,12-Pentacosadiynoic Acid Self-assembled Thin Films on Ag Surfaces

Jong Kuk Lim,[1] Yunhee Lee,[2] Kangtaek Lee,[2] Myoungseon Gong,[3] and Sang-Woo Joo*[4]
[1]*Department of Chemistry, Northwestern University, Evanston Illinois 60208, U.S.A.*
[2]*Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea*
[3]*Department of Chemistry, Dankook University, Cheonan 330-714, Korea*
[4]*Department of Chemistry, Soongsil University, Seoul 156-743, Korea*

(Received July 31, 2007; CL-070810; E-mail: sjoo@ssu.ac.kr)

Molecular architecture of the self-assembled thin films of 10,12-pentacosadiynoic acid (PCDA) anchoring on Ag surfaces via its carboxylate group appeared to have a reversible thermochromic disordered-to-regular trans-zigzag transition at ≈65 °C by an external reflectance infrared spectroscopy and surface-enhanced Raman scattering study.

Stimuli-responsive materials are of widespread fundamental interest because of their potential applications such as rapid detection of dangerous biological agents[1] and highly dense information storage.[2] Since works on the solid-state polymerization of diacetylene and polydiacetylene chemistry and physics have become an integral part of modern polymer science,[3,4] researchers have reported that heat, pH, UV, or γ-ray irradiation can induce polymerization of diacetylene derivatives.[5–10] The polymerization of diacetylene has been known to result in the formation of a deep blue color ($\lambda_{\max} \approx 625$ nm, blue phase) that changes to an intense purple-red color ($\lambda_{\max} \approx 540$ nm, red phase). This thermochromic transition has been harnessed for the purpose of chemical and biological sensors.[11,12]

Ultrathin films have received much attention owing to their potential applications in electronic devices, colorimetric sensors, and surface-sensitive probes.[13] Temperature-dependent spectral behavior on surfaces can provide the energetics or phase transition of adsorbates on metal surfaces.[14–16] Ag powder substrates have an advantage of investigating self-assembled monolayers (SAMs) on their surfaces by applying both surface infrared and Raman spectroscopy for the identical sample in a simultaneous way.[17] Although several spectroscopic works[6–8] were reported, there has been no study on the thermochroism and the resulting molecular architecture change of a diacetylene derivative film fabricated on metal surfaces to the best of our knowledge.

In this work, to better understand interfacial structure and thermochroism of diacetylene materials, we performed a temperature-dependent infrared and Raman study of 10,12-pentacosadiynoic acid (PCDA) self-assembled monolayers (SAMs) adsorbed on Ag powder surfaces. The purpose of this study is to better understand the molecular architecture and reversible thermochroism of the diacetylene SAMs on Ag.

Figure 1a shows an external reflection spectrum of PCDA in its solid state. The vibrational bands at 1693, 1462, and 1419 cm^{-1} can be ascribed to the C=O stretching, CH$_2$ scissoring, and C–O stretching mode, respectively. The two vibrational bands at 2847 and 2917 cm^{-1} can be assigned to the symmetric and antisymmetric CH$_2$ stretching bands, respectively. Although not clearly seen as in the previous report,[7] the C≡C stretching bands were scarcely observed at ≈2147 cm^{-1} in the infrared spectra.

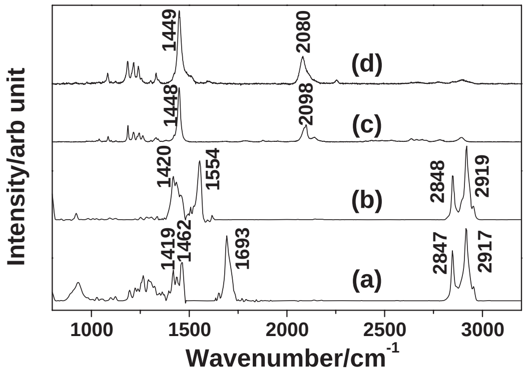

Figure 1. Infrared spectra of PCDA in (a) its solid state and (b) after the assembly on Ag powder surfaces. Raman spectra of polyPCDA in (c) its solid state and (d) after the assembly on Ag powder surfaces. The intensity obtained at room temperature (ca. 25 °C) is normalized with respect to the strongest bands at each spectrum for a better comparison.

Upon adsorption on Ag as shown in Figure 1b, it is noteworthy that the C=O vibrational band disappeared and that the two bands due to the antisymmetric and symmetric ν (COO$^-$) modes were found at 1554 and 1420 cm^{-1}, respectively. These results clearly indicate that PCDA should adsorb on Ag powder surfaces via its carboxylate form.

In the OR (ordinary Raman) spectrum of polyPCDA shown in Figure 1c, the bands associated with the CH$_2$ rocking, wagging or twisting, and antisymmetric stretching vibrational modes can be found at 692, 1040–1380, ≈2893 cm^{-1}. The prominent vibrational bands at 1448 and 2098 cm^{-1} can be assigned to the ν (C=C) and ν (C≡C) bands, respectively.[8] These spectral positions are in good agreement with the data[6] obtained at 633 nm but lower than those at 488 and 514 nm.[8] This spectral shift can be interpreted as a resonance effect with the π-electron delocalization.[6] We could observe the C=C stretching bands in Raman spectra presumably because of the polymerization via a laser irradiation. In Figure 1d of the SERS spectrum, the C=C stretching band was found to be almost unchanged, but the C≡C stretching band was observed to be red-shifted by ≈18 cm^{-1}. This may suggest a parallel orientation of the C≡C stretching band and a perpendicular stance of the C=C band from the electromagnetic SERS selection rule.

As shown in Figure 2a, it is noteworthy that the ν (C=C) bands in the SERS spectra change with temperature. For the OR spectrum, we could observe the blue color crystal turned

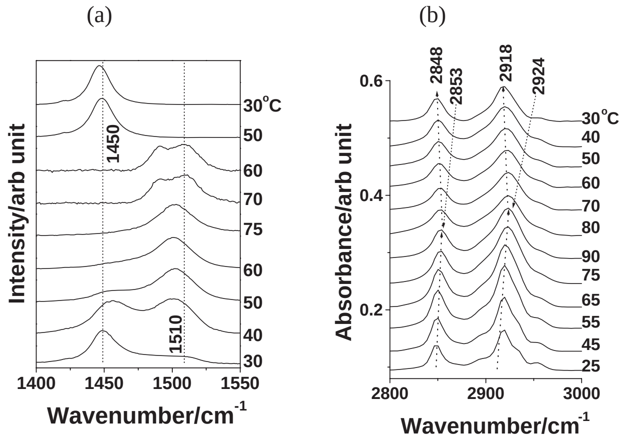

Figure 2. (a) SERS Raman spectra of adsorbed PCDA on Ag powders in increasing temperature at 30, 40, 50, 60, 75 °C and decreasing temperature 70, 60, 50, 30 °C. (b) External reflection infrared spectra of PCDA on Ag powders taken in increasing temperature at 25, 45, 55, 65, 75, 90 °C and decreasing temperature at 80, 70, 60, 50, 40, 30 °C. The spectral intensity is normalized at each temperature for a better comparison.

reddish at this temperature. To examine the molecular architecture change on the surface in a more careful way, we performed a temperature-dependent infrared study on Ag powder surfaces. As shown in Figure 2b, the CH$_2$ symmetric and antisymmetric stretching vibrational modes were found to be shifted from 2848 and 2918 cm^{-1} at room temperature to 2853 and 2924 cm^{-1}, respectively. These results indicate a rather disordered structure above the transition temperature. The blue phase with a regular trans-zigzag structure of their trans alkyl side chains appeared to transform to the red phase of an irregular structure containing gauche conformations as a structural disorder of the side chain group.[6] The transition of the blue phase with a regular trans-zigzag structure of their trans alkyl side chains proceeds to the red phase of an irregular structure containing gauche conformations.[8]

These changes were found to be reversible by heating and cooling the temperature. Figure 3 illustrates a schematic diagram of the reversible thermochromic architecture change for PCDA self-assembled layer on Ag below and above $\approx$65 °C. The CH$_2$ bands were red-shifted by ca. 6 cm^{-1} as the temperature was lowered. This result may support a trans-zigzag structure at lower temperature as depicted in Figure 3. Above the transition temperature, a disordered form should exist on surfaces. Also a surface coverage is expected to be lower at higher temperatures as discussed in our recent study.[18] The driving force for this reorganization from the disordered to the ordered state is assumed to be the substantial van der Waals interaction between the alkyl chains below the transition temperature.[4] Our spectroscopic study shall be useful in fabricating a thermo-responsive thin film on metal surfaces by understanding its structural change.

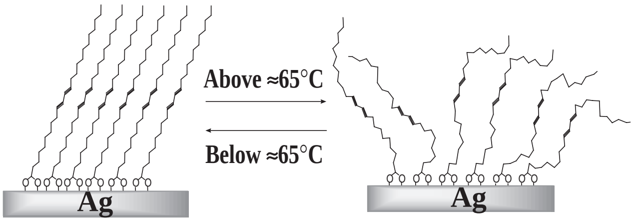

Figure 3. Schematic diagram of the reversible thermochromic architecture change for PCDA self-assembled layer on Ag below and above $\approx$65 °C.

S-W.J. thanks Mr. Bum Keun Yoo for helping experiments and Prof. Dong June Ahn for valuable discussion. This work was supported by the Soongsil University Research Fund.

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19 PCDA (>98%) was purchased from Fluka. The Ag powder (99.9+% purity) with a nominal particle size of 2–3.5 µm was purchased from Aldrich.[17] We chose to use not a flat substrate but a powder surface, since both surface infrared and Raman spectra can be obtained for the same sample. We also tested the SERS spectra of PCDA on roughed Ag plate surfaces (see ref 20). For the self-assembly of PCDA on Ag, approximately 0.050 g of silver power was placed in a cleaned small vial into which stock solution of 10 mM PCDA and the same molar amount of NaOH were added and left overnight. A portion of the PCDA-assembled powdered sample was transferred onto a ZnSe crystal of Pike Technology Miracle external reflection accessory equipped with a temperature controller. UV–vis absorption spectra of PCDA, λ_{max}'s for the red and blue phases were observed at $\approx$543 and $\approx$625 nm, respectively, were obtained with a Shimadzu UV-3101PC spectrophotometer. The infrared spectra were obtained using a FT-IR spectrometer with a maximum resolution of 0.09 cm^{-1} (Thermo Nicolet 6700). Raman spectra were obtained using a Renishaw Raman confocal system model 1000 spectrometer. The 632.8 nm irradiation from a 20 mW air-cooled HeNe laser (Melles Griot Model 25 LHP 928) with a resolution of 1 cm^{-1} were used as the excitation sources for the Raman experiments using a Linkam THMS 600 thermal heating stage. Since we have not introduced the UV light to attempt any intentional polymerization, the sample is not assumed to be substantially polymerized except the Raman measured ones irradiated by a high power laser.
20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) September 8, 2007; doi:10.1246/cl.2007.1226