Raman Microspectroscopic Study on Polymerization and Degradation Processes of a Diacetylene Derivative at Surface Enhanced Raman Scattering Active Substrates. 1. Reaction Kinetics

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Received: May 20, 2004; In Final Form: September 1, 2004

Raman microspectroscopy was applied to study the polymerization kinetics of the Langmuir−Blodgett (LB) films of 10,12-pentacosadiynoic acid (DA) adsorbed on surface enhanced Raman scattering (SERS) active Ag island films. A two-dimensional (2D) Raman microscopic image measured at 1520 cm^{-1} exhibits bright and dim spots with the diameter of several hundred nanometers. Raman microscopic spectra, measured by defocusing the excitation laser light (532 nm, diameter of ca. 10 μm) on the samples at room temperature, proved the occurence of the surface processes consisting of the formation of polydiacetylene (PDA) in the blue phase, its conversion to the red phase, and subsequent bleaching. These reactions were negligible under the same condition for the DA-LB films prepared on a smooth (i.e., SERS-inactive) Ag film, indicating that the 532-nm-induced polymerization and the bleaching process are enhanced by the SERS-active substrates. At low temperatures below −50 °C, the Raman microscopic measurements proved the formation of the blue phase and its conversion to the red phase with much lower reaction rates compared to the corresponding rates at room temperature. The bleaching, however, was much suppressed at the low temperatures. The kinetic analyses of the formation of the blue phase and its conversion to the red phase were performed by using the intensity changes of the Raman bands due to the blue (1477 cm^{-1}) and red (1517 cm^{-1}) phases as a function of the irradiation time. The results strongly suggested the existence of at least two processes taking place simultaneously on the SERS-active substrates; that is, one of the processes is a sequential reaction, DA−monomers → PDA in the blue phase → PDA in the red phase, and the other is another sequential reaction, DA−monomers → PDA in the red phase → degradation species (probably amorphous carbon). Thus, even at the low temperatures, there occurs the surface reaction consisting of the formation of PDA and its degradation. The reaction can be ascribed to a process taking place at the highly SERS-active site, which gives the bright spot (so-called "hot spot") on the 2D Raman image, as proved by the confocal Raman microscopic measurement in the following paper.

Introduction

It is a well-known fact that heat-, UV-, and γ-ray-irradiation-induced polymerization of a variety of substituted diacetylene derivatives forming single crystals as well as Langmuir−Blodgett (LB) films proceeds via a 1,4-addition reaction to a fully conjugated polydiacetylene.[1] A unique feature of the polymerization is that it proceeds keeping the geometrical integrity of the monomers in the solid states; thus, the polymerization of the single crystal leads to the perfect single crystal of the corresponding polydiacetylene, and the polymerization of the LB film proceeds with retention of the LB assembly. The polymerization of the LB films of long-chain diacetylene monocarboxylic acids such as 10,12-pentacosadiynoic acid $(CH_3(CH_2)_{11}C\equiv C-C\equiv C(CH_2)_8COOH$, DA) has been studied by various methods including X-ray diffraction,[2] UV−vis absorption spectroscopy,[2−4,6,7,9−11] resonance Raman scattering (RRS), and surface enhanced Raman scattering (SERS) spectroscopies.[3,5,9−12] The polymerization of the LB films of DA (DA-LB) results at first in the formation of a deep blue

color ($\lambda_{max} \approx 635$ nm, "blue phase"), which changes into an intense purple-red color ($\lambda_{max} \approx 540$ nm, "red phase") under the continuous UV and γ-ray irradiation. The color transition can be interpreted as a result of a change in electronic states. Mino et al.[6] studied the color change by using UV−vis and IR spectroscopies and explained the change as resulting from an onset of fluctuation and/or a structural disorder of the side chain groups linked to the polydiacetylene (PDA) backbone. Saito et al.[9] also applied absorption, infrared reflection absorption, and RRS spectroscopies to study the UV-irradiation-induced polymerization of the DA-LB film prepared on a flat silver substrate, indicating that the polymerization proceeds through two steps, being almost completed in the first step. The blue phase formation proceeds in the first step, in which the polymer backbone keeps a regular trans-zigzag structure with the all-trans alkyl side chains. In the second step, the regular structure is converted to an irregular one containing gauche conformations in the alkyl side chains. The conversion accompanies the shifts of RRS bands near 2080 (due to a $C\equiv C$ stretching) and 1485 cm^{-1} (due to a $C=C$ stretching) for the blue phase to the corresponding RRS bands near 2100 and 1515 cm^{-1} for the red phase; the higher frequency shifts of the $C\equiv C$ and $C=C$ stretching bands were interpreted as a result of an interruption

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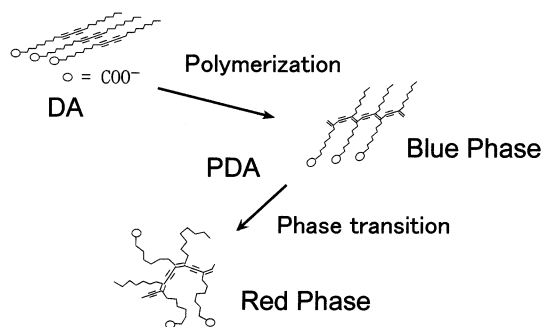
Figure 1. Schematic representation of the polymerization process of the DA-LB film. See text.

of the fully extended PDA backbone or as a result of a reduction of the average conjugation length. Figure 1 is a schematic representation of the polymerization process of DA-LB revealed by the RRS spectroscopy. The UV-irradiation-induced polymerization of the DA-LB monolayer prepared on a SERS-active silver island film has been extensively studied by Shirai et al. by using the SERS spectroscopy.[11] The result indicated that the polymerization rate is remarkably larger than that of the multilayered LB film of DA on the smooth silver (SERS-inactive) film; the polymerization, however, proceeds in a similar way to that of the multilayered film, exhibiting the transition from the blue to red phase.

In this paper we measured the SERS spectra of the DA-LB films prepared on various SERS-active silver island films by using Raman microscopic methods and found that, when the excitation laser light (532 nm) is focused with the diameter smaller than about 10μm, the polymerization proceeds without the UV- or γ-irradiation at room temperature. In addition, upon a tight focus of the excitation laser light to submicrometers in diameter and irradiation of a SERS-active site directly, the observed SERS spectra exhibited remarkable spectral fluctuations ascribable to surface chemistry associated with the formation of amorphous carbon from PDA under the irradiation of the focused laser light. The present paper (part 1) describes the SERS spectroscopic study of the 532-nm excitation light-induced polymerization of the DA-LB films at low temperatures to elucidate the polymerization kinetics of the DA monomers on the SERS-active substrates. In the following paper (part 2), the fluctuations of the SERS spectra of the DA-LB films on SERS-active silver films are reported to clarify the surface chemistry taking place at SERS-active or so-called "hot spot" on the silver films.

Experimental Section

Materials. DA was purchased from Wako Pure Chemicals Co. Ltd. and used as received. Ag (99.999%) was obtained from Kojundo Chemical Labolatory.

Preparation of DA-LB Films. The DA-LB films were prepared by using a Kyowa Kaimen Kagaku, HBM-AP2, Langmuir trough with a Wilhelmy balance in a similar way as that already reported.[9,11] Water used for the preparation was purified with a Millipore Inc. Milli-A Plus water purifier. A CdCl$_2$ solution was added to the trough to a level of 2×10^{-4} mol/L at pH 6.8 (adjusted with NaHCO$_3$) in order to convert DA to the corresponding cadmium salt. A DA solution in chloroform (2×10^{-3} mol/L) was spread on the trough water and transferred to a substrate by a vertical dipping method at a surface pressure of 20 mN/m and at ca. 20 °C.

Preparation of SERS-Active Substrates. Two kinds of substrates were prepared. One of the substrates was prepared

by a vacuum evaporation of Ag on a freshly cleaved mica plate kept at 120 °C with a mass thickness of 6 nm, which was monitored by a microbalance (ULVAC Japan Ltd., model CRTM-5000). The other one was electrochemically prepared on an indium−tin oxide coated glass plate (ITO) from a silver nitrate solution (0.1 mmol/L) using a potentiostatic pulse method, where a static electrode potential of −500 mV (vs Ag/AgCl reference electrode) was applied to the ITO electrode for 300 mV and then kept at 0 V for 30 min. The number of the LB films prepared on the substrates was fixed at five, and the DA-LB film samples prepared on the mica and ITO substrates were denoted as DA-LB($n = 5$)/Ag island/mica and DA-LB($n = 5$)/Ag island/ITO, respectively.

SERS Spectral Measurement. Raman microscopic measurements were performed with a homemade Raman microscope consisting of a Kaiser Optical Holospec (f/1.8) spectrometer equipped with a supernotch filter (for 532 nm), a multichannel detector (Priceton Instruments Inc., CCD-1100-PB), an Olympus BH2-UMA microscope, and a CW Nd:YAG laser(Coherent Co. Inc., DPSS-532) as an excitation source. An objective (50×, NA 0.55) was used to provide a diffused spot size of ca. 10 μm in diameter. The laser power was reduced to ca. 23 μW at the sample point in order to eliminate any change in the surface morphology of the SERS-active substrate and to keep the bleaching of the DA-LB samples as small as possible. (The elimination of the surface morphology change was confirmed by observing the absence of SERS spectral change of cupper phthalocyanine on the SERS-active substrates under prolonged illumination of the excitation light.) The accumulation time of the measurement was fixed at 2 s. The substrate temperature was controlled by using a temperature controller of a microscope stage (Japan Hitech Co. Ltd., LK-600PM). Two-dimensional (2D) SERS microscopic images of the DA-LB films on the SERS-active substrates were measured by using a confocal Raman microscope (Tokyo Instruments Co. Ltd, Nanofinder 30) with a lateral spatial resolution of ca. 0.25 μm for a microscope objective lens (100×, NA 0.9) and the excitation laser light at 488 nm (laser power ca. 5 μW).

Results and Discussion

SERS Spectroscopic Images of DA-LB($n = 1$)/Ag Island/ ITO and DA-LB($n = 1$)/Ag Island/Mica. Figure 2, parts A and B, exhibits the 2D Raman microspectroscopic images of DA-LB($n = 1$)/Ag island/ITO and DA-LB($n = 1$)/Ag island/ mica, respectively, which were measured at 1520 cm^{-1}. Each image consists of bright and dim spots with diameters of submicrometer ranges on the dark background. As explained in the following section, upon irradiation with the 532 nm laser line at room temperature, the DA-LB film is immediately converted to PDA. The bright spots are ascribable to PDA residing at highly SERS-active Ag islands, which, presumably, correspond to so-called "hot spots", and the dim spots are ascribable to PDA residing at Ag islands with relatively low SERS activity. The images observed for DA-LB($n = 5$) are more or less similar to those shown in Figure 2.

SERS Spectra of DA-LB($n = 5$)/Ag Island/ITO and DA-LB($n = 5$)/Ag Island/Mica. Figures 3 and 4 illustrate the SERS spectra in the 1600−1400 cm^{-1} region observed for DA-LB($n = 5$)/Ag island/ITO and DA-LB($n = 5$)/Ag island/mica, respectively, as a function of the 532 nm light irradiation time at various temperatures. The laser spot was defocused to a diameter of ca. 10 μm. Then, the spectral changes observed in Figures 3 and 4 are associated with average surface chemistry taking place at SERS-active sites including the bright and dim
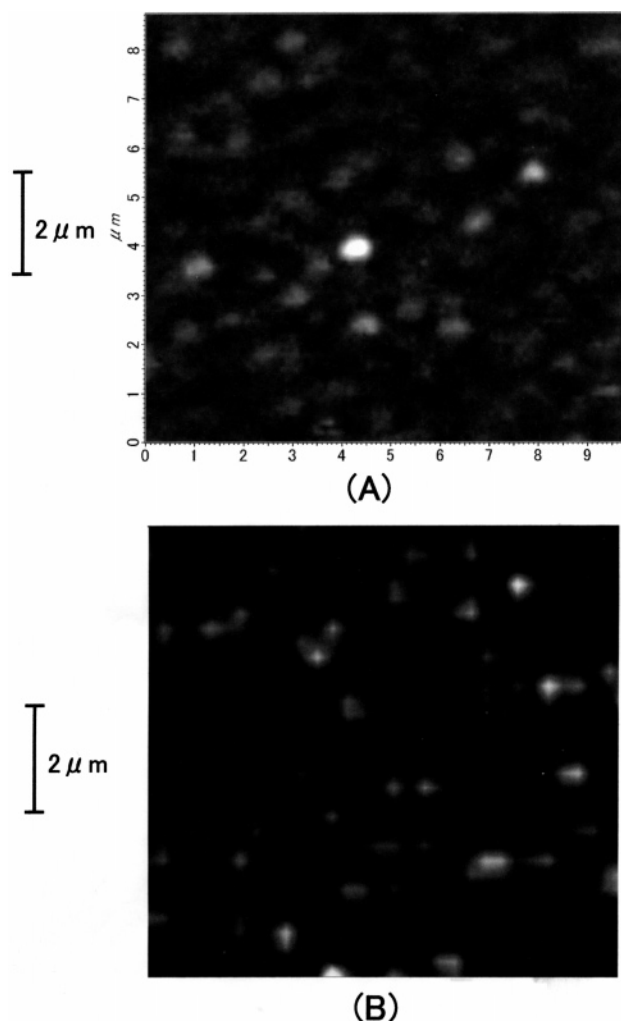
Figure 2. Confocal SERS microscopic images of the DA-LB($n = 5$) film on the Ag island film/ITO (A) and the film on the Ag island/mica (B) measured at 1520 cm^{-1} (excitation wavelength, 488.0 nm; laser power, ca. 5 μW).

spots and the dark background. The SERS spectral measurements were performed also on DA-LB($n = 1$) adsorbed on the SERS-active substrates, giving similar spectral changes to those seen in Figures 3 and 4. The S/N ratios in the former spectra, however, were much poorer than those of the latter spectra. So, we confine the results for the DA-LB($n = 5$) samples in the following: The bands around 1517 and 1475 cm^{-1} in Figures 3 and 4 are due to the C=C stretching vibrations of the red and blue phases, respectively.[9,11] Figures 3A and 4A indicate that upon irradiation of the excitation beam at the room temperature the DA-LB films on the ITO and mica substrates are immediately converted to PDA in the blue phase, which is subsequently transformed to the red phase. The 1517 cm^{-1} band due to the red phase begins to reduce its intensity after ca. 5 min of the irradiation on both substrates, indicating that degradation or bleaching of PDA takes place. At −50 °C (Figures 3B and 4B) the blue phase is immediately formed and converted to the red phase under the irradiation of the 532 nm light. Even after 60 min of irradiation, however, the 1517 cm^{-1} band due to the red phase does not reduce its intensity on both substrates, indicating that the degradation is appreciably suppressed at −50 °C. At −100 °C (Figures 3C and 4C) the blue phase, which does not appear on the initial irradiation, steadily increases under the continuous irradiation. The conversion to the red phase on the ITO substrate is not detected after 60 min

of the irradiation, while the conversion is observed on the mica substrate, although the conversion is much retarded in comparison to that on the ITO and mica substrates at −50 °C. The spectral changes at −200 °C (Figures 3D and 4D) are appreciably different from those observed at the substrate temperatures above −100 °C; for example, the C=C stretching band is observed at 1470 cm^{-1}, which is appreciably lower than that due to the blue phase (1477 cm^{-1}), and the corresponding bands are observed at 1475 and 1448 cm^{-1} for the mica substrate. Presumably, these spectral features are ascribable to oligomers trapped as intermediates of the polymerization initiated by the irradiation at 532 nm.

Reaction Kinetics. The Raman microscopic measurements performed on the DA-LB($n = 5$) film on a flat (SERS-inactive) Ag film (with the mass thickness of ca. 100 nm) at ca. 20 °C indicate that after several minutes of the excitation laser light irradiation there appears a 1479 cm^{-1} band due to PDA in the blue phase, although the intensity of the band is much smaller than those of the corresponding bands in Figures 3A and 4A. The Raman microscopic measurements performed on the DA-LB film at the flat Ag substrate at lower temperatures below −50 °C do not show any spectral change indicative of the formation of PDA under prolonged irradiation at 532 nm. These results suggest that the polymerization rate is appreciably enhanced on the SERS-active substrates, as in the case of the UV-irradiation-induced polymerization of the DA-LB films on a SERS-active substrate.[11] To analyze the process quantitatively, the dependence of the SERS spectral changes on the substrate temperature was extensively studied in the temperature range of −50 to −70 °C. The Gaussian curves are assumed to resolve the SERS bands associated with the blue (ca. 1475 cm^{-1}) and red phases (ca. 1517 cm^{-1}), and the peak intensities of both peaks are plotted as a function of the irradiation time in the 0−200 s range. Figure 5, parts A and B, illustrates the results for DA-LB($n = 5$)/Ag island/ITO at −50 and −60 °C, respectively, and Figure 5, parts C and D, illustrates the results for DA-LB($n = 5$)/Ag island/mica at −50 and −60 °C, respectively. As can be seen from the figure, the peak intensities due to the blue phase maximize at ca. 10 s of the irradiation time and then steadily decrease, while the intensities due to the red phase continue to increase exhibiting the turning point from a fast- to low-increasing rate at ca. 20 s of the irradiation. The spectral changes observed for the LB films on both substrates measured at other temperatures in the range of −50 to −70 °C are more or less similar to those shown in Figure 5.

The evolution curves for the blue phase at an initial step (the irradiation time range of 0−150 s) in Figure 5 are indicative of a successive unimolecular reaction, which can be expressed as follows:

$$M \xrightarrow{k_1} B \xrightarrow{k_2} R \tag{1}$$

where M denotes the reactive monomer formed on the irradiation at 532 nm, B denotes the blue phase and R denotes the red phase, and k_i's are the corresponding reaction rate constants. We are concerned only with the polymerization at low temperatures below −50 °C, and for a moment, the degradation of PDA is not considered in the scheme. The rate constants are assumed to be constant at a fixed temperature, because, as Figures 3 and 4 show, the Raman bands due to the blue and red phases do not show any frequency change, indicating that each phase can be treated as a chemical identity as a whole. Actually, the reaction scheme shown in eq 1 has been successively assumed to explain the polymerization processes of
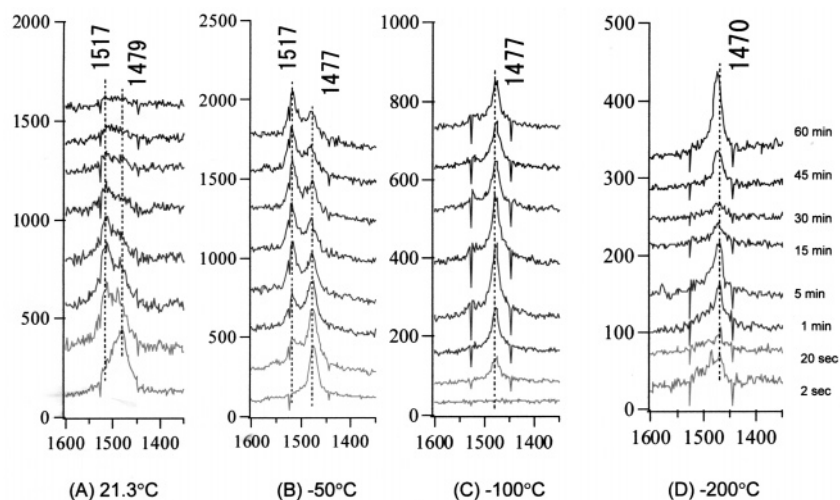
Figure 3. Microscopic SERS spectra of DA-LB($n = 5$)/Ag island/ITO as a function of the 532 nm irradiation time at various temperatures. The irradiation times are indicated at the right-hand side of the figure. The laser power was fixed at 23 μW at the sample spot, and the accumulation time of each spectrum was 2 s.
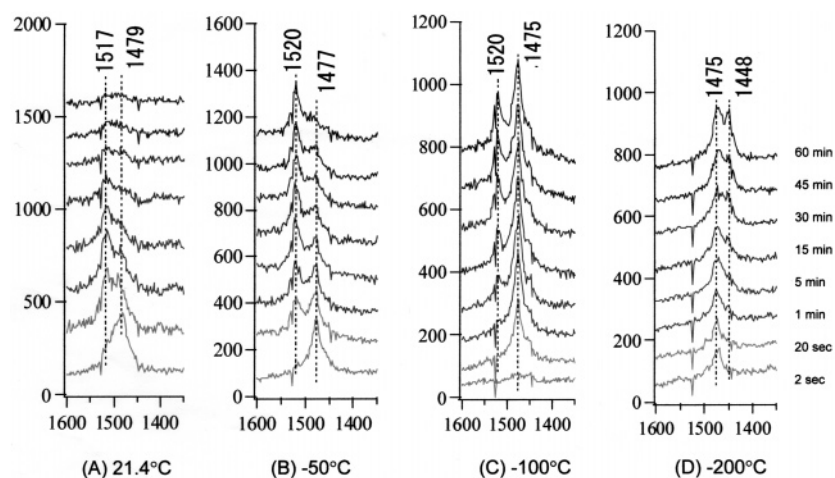
Figure 4. Microscopic SERS spectra of DA-LB($n = 5$)/Ag island/mica as a function of the 532 nm irradiation time at various temperatures. The irradiation times are indicated at the right-hand side of the figure. The laser power was fixed at 23 μW at the sample spot, and the accumulation time of each spectrum was 2 s.

diacetylene derivatives on the air−water interface[12] and on solid substrates.[13] The rate equations of the consecutive first-order process can be solved as follows:

$$[B] = \frac{k_1[M_0]}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{2}$$

$$[R] = \frac{k_1 k_2 [M_0]}{k_2 - k_1}\left(\frac{e^{-k_2 t}}{k_2} - \frac{e^{-k_1 t}}{k_1}\right) + [M_0] \tag{3}$$

where $[M_0]$ is the initial population of the reactive monomer, $[B]$ and $[R]$ are the populations of the blue and red phases, respectively, as a function of the irradiation time. The peak intensities of the Raman bands at 1477 and 1517 cm^{-1} in Figures 3 and 4 are proportional to $[B]$ and $[R]$, respectively. Introducing the proportionality constants parametrically, the time courses of the intensity changes of the Raman bands due to the blue phase observed at the substrate temperature range of −50 to −70 °C are simulated by using eq 2 to determine the rate constants, which are summarized in Table 1. The calculated curves for the intensity changes versus the irradiation time are plotted by the solid lines in Figure 5, which reproduce the experimental results appreciably well. The kinetic parameters,

k_1 and k_2, are temperature-dependent and allow us to determine the activation energies for the formation of the blue phase as well as the blue to red phase transitions, as explained below. The time course of the intensity changes of the Raman bands associated with the red phase is also simulated by using eq 3 and the time constants determined above. In the simulation, it was assumed that the intensities of the Raman bands observed after ca. 180 s of the irradiation are ascribed only to the red phase that originated from the blue phase via the reaction scheme shown in eq 1, which allows us to automatically determine the relative proportional factors. Although the results of the simulation, which are shown by the dotted lines in Figure 5, reproduce the intensity changes observed after ca. 180 s, they deviate largely from the experimental results in the time range of 0−150 s, suggesting the existence of a second process occurring mainly at the initial stage of the irradiation. As explained in the following paper, the DA monomers adsorbed on highly SERS-active sites (or so-called "hot spots") are converted to the red phase promptly upon the onset of the irradiation at 488 nm, which is successively bleached to form amorphous carbon. The hot spot accelerates the polymerization of the DA monomers as well as the bleaching of PDA. Then, the second process may be explained by considering that a part of the monomers
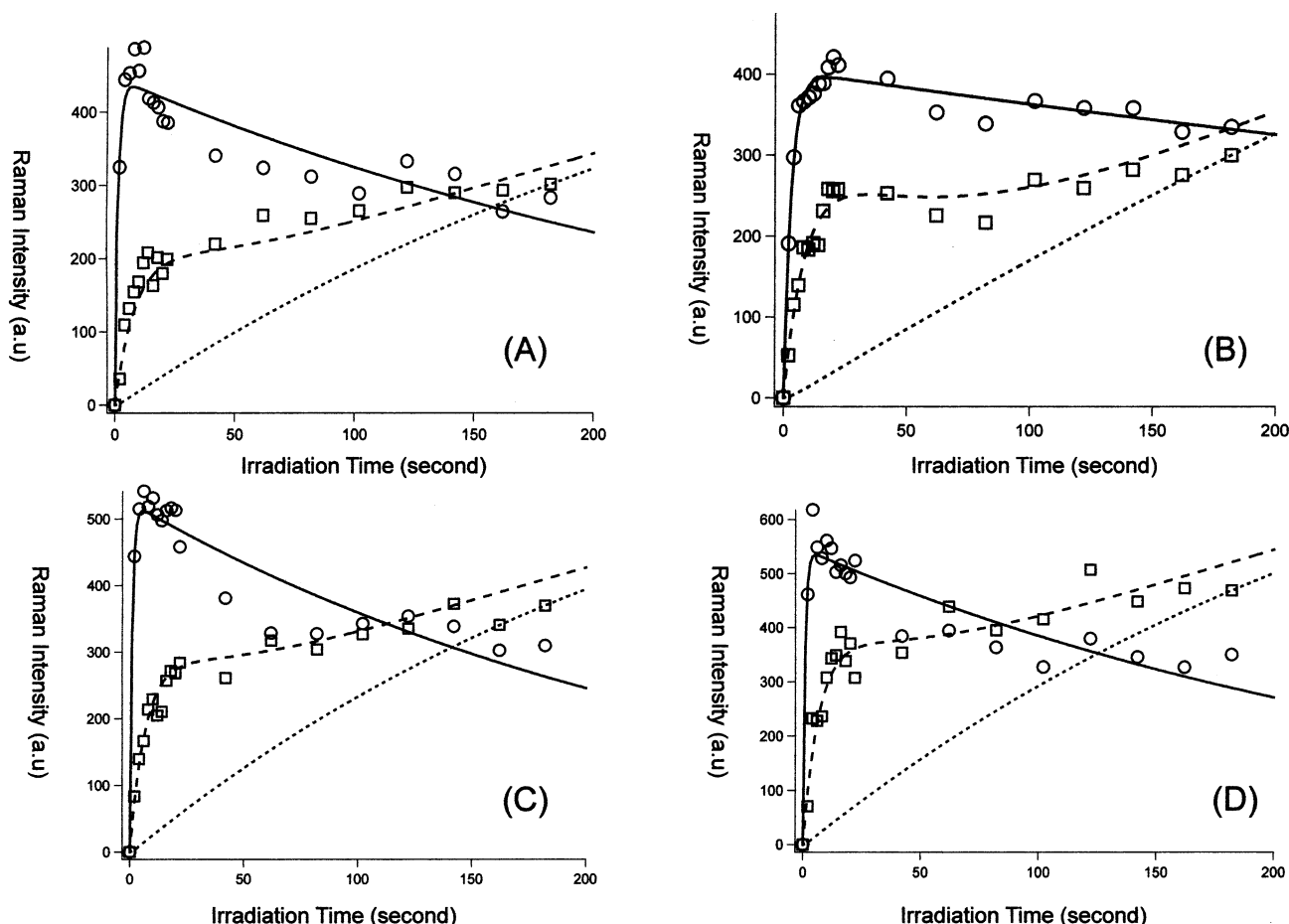
Figure 5. Intensities of the 1517 (□, red phase) and 1477 cm^{-1} bands (○, blue phase) as a function of irradiation time at 532 nm measured for DA-LB($n = 5$)/Ag island/ITO (A) and DA-LB($n = 5$)/Ag island/mica (C) at −50 °C and for DA-LB($n = 5$)/Ag island/ITO (B) and DA-LB($n = 5$)/Ag island/mica (D) at −60 °C: solid line, the intensity change of the Raman band due to the blue phase as a function of the irradiation time calculated by assuming the reaction scheme in eq 1; dotted line, the intensity change of the Raman band due to the red phase calculated by assuming the scheme in eq 1; dashed line, the intensity change of the Raman band due to the red phase calculated by assuming both of the schemes in eqs 1 and 4. See text.

TABLE 1: Reaction Rates of Blue Phase Formation (k_1) and Blue-to-Red Phase Transition (k_2)

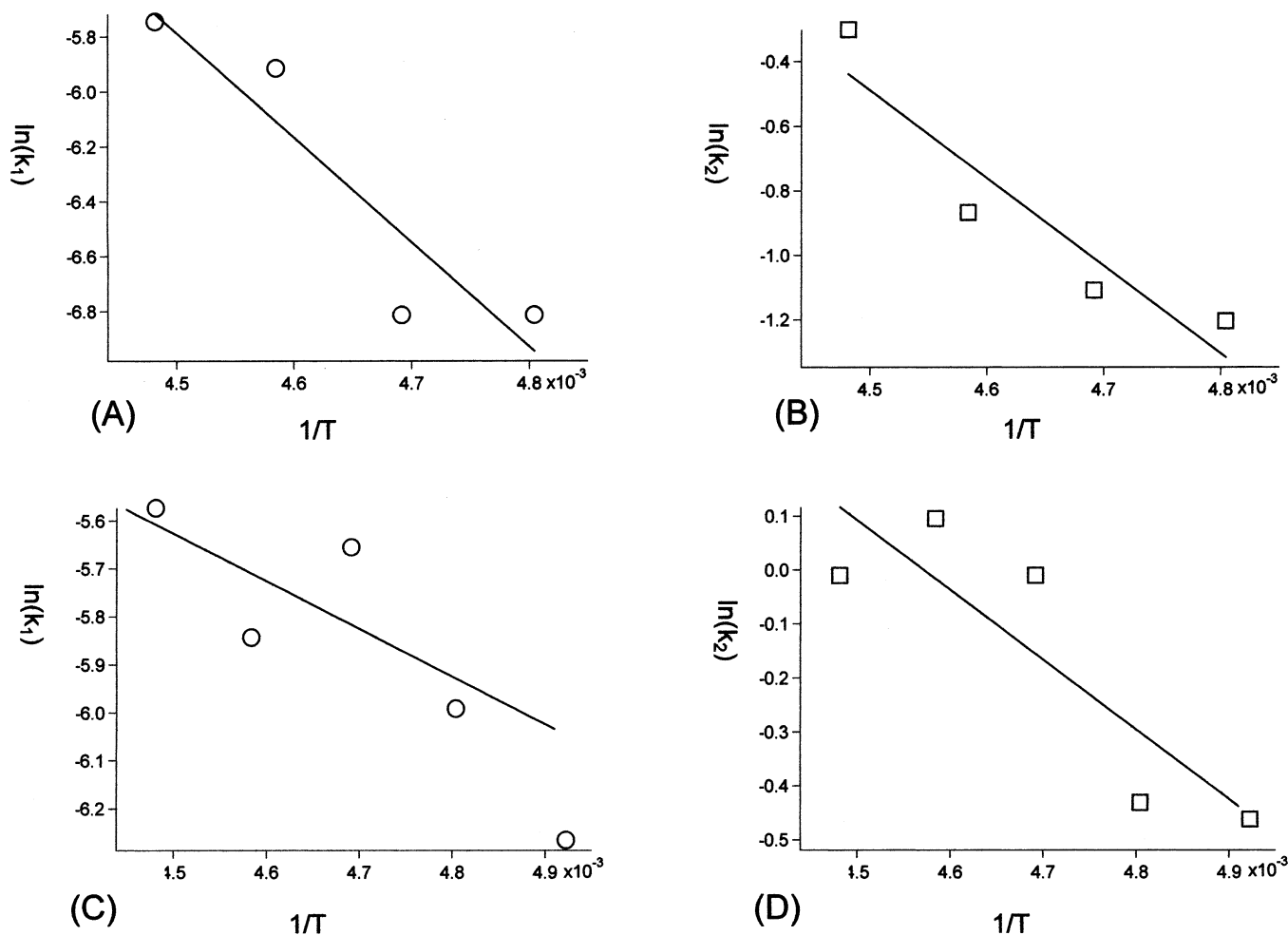|	DA-LB($n = 5$)/Ag island/ITO		DA-LB($n = 5$)/Ag island/mica	
T (K)	k_1 (s^{-1})	k_2 (s^{-1})	k_1 (s^{-1})	k_2 (s^{-1})
223.15	3.2×10^{-3}	7.4×10^{-1}	3.8×10^{-3}	9.9×10^{-1}
218.15	2.7×10^{-3}	4.2×10^{-1}	2.9×10^{-3}	11.0×10^{-1}
213.15	1.1×10^{-3}	3.3×10^{-1}	3.5×10^{-3}	9.9×10^{-1}
208.15	1.1×10^{-3}	3.0×10^{-1}	2.5×10^{-3}	6.5×10^{-1}
203.15			1.9×10^{-3}	6.3×10^{-1}

adsorbed on the hot spot undergo the immediate formation of the red phase and the successive degradation even at the low temperatures below −50 °C, which can be expressed in the following scheme:

$$M' \xrightarrow{k_3} R' \xrightarrow{k_4} D \qquad (4)$$

where M′ is the DA monomer activated on the hot spot, R′ is the red phase directly formed from the monomer on the hot spot, and D is the degradation product. [R′] is expressed by eq 2, where k_1 and k_2 are replaced by k_3 and k_4, respectively. By using the equation and the relative proportionality factor, we can simulate the Raman band intensity due to the red phase (ca. 1517 cm^{-1}) produced through the reaction in eq 4, indicating that, in contrast to the case of the kinetic parameters, k_1 and k_2, the values of k_3 and k_4 are almost temperature-independent to be 0.012 ± 0.002 and 0.12 ± 0.04, respectively, for DA-LB($n = 5$)/Ag island/ITO, and 0.011 ± 0.002 and 0.15 ± 0.02,

respectively, for DA-LB($n = 5$)/Ag island/mica. The dashed lines in Figure 5 are the calculated sum of the Raman intensities associated with the red phases produced by the two processes 1 and 4, the contributions from the latter process being calculated by using the average kinetic parameters. The results of the calculation are reasonably in good fits to the time courses of the Raman intensities of the red phase for both substrates.

Thus, the analyses of the SERS spectral changes observed for both SERS-active substrates at the temperature range of −50 to −70 °C strongly suggest the existence of at least two kinetic processes for the polymerization of the DA monomer on the SERS-active substrates. The first process proceeds at the sites with relatively low SERS activity (probably the dark background of the 2D Raman microscopic image in Figure 2), where the DA monomers undergo the polymerization following the scheme in eq 1, and the second process proceeds at the hot spot, where the immediate formation of the red phase and subsequent degradation take place (the scheme in eq 4). The activation energies for the formation of the blue phase and those for the blue to red phase transition in the first process are determined from the Arrhenius plots, which are illustrated in Figure 6. From the plots, the activation enthalpies for the blue phase formation (ΔH_1) and the blue to red phase transition (ΔH_2) are determined to be 31.6 ± 9.2 and 22.6 ± 6.2 kJ/mol, respectively, for DA-LB($n = 5$)/Ag island/ITO and 8.2 ± 5.4 and 10.7 ± 6.3 kJ/mol, respectively, for DA-LB($n = 5$)/Ag island/mica. We note that the activation energies for the ITO substrate are appreciably

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Figure 6. Arrhenius plots of the rate constants, k_1 (○) and k_2 (□): (A, B) DA-LB($n = 5$)/Ag island/ITO; (C, D) DA-LB($n = 5$)/Ag island/mica. See text.

larger than those for the mica substrate, which corresponds to the difference in the spectral changes observed for both substrates at -100 °C (Figure 3C and Figure 4C). Although the SERS images from both substrates (Figure 2) are similar to each other, preliminary AFM observations (not shown in the present paper) indicate that the mica substrate consists of more or less regular silver spheres, while the ITO substrate comprises irregular bumps of silver. The arrangement of DA-LB on the mica substrate may be more favorable for the formation of the blue phase and its conversion to the red phase than the arrangement on the ITO substrate.

It is known that the thermal polymerization of diacetylene derivatives in the solid state takes place above room temerature.[14,15] Although the explicit mechanism has not always been clarified, the results indicate that phonons generated thermally are sufficient to trigger the polymerization process.[16] The ESR spectra of a partially polymerized diacetylene derivative at 60 °C proved the existence of a triplet radical (or a carbene) as an intermediate species of the polymerization.[15] On the other hand, theoretical[17,18] as well as experimental studies[19-21] have been performed on the enhancement of photochemical processes on SERS-active substrates under the illumination of excitation laser lights, which are ascribable to enhanced absorption through the huge electromagnetic field at surface protrusions on the substrates. Goncher et al.[19] and Wolkow and Moskovits,[20] who studied the enhanced photofragmentation reactions of simple aromatic molecules such as pyrazine on roughened silver surfaces under illumination of near-UV and visible laser light, concluded that the reactions are initiated by a two-photon

process. It is also possible that the excitation energy, acquired by an enhanced absorption of an adsorbate on SERS-active substrates, is dissipated through nonradiative decay by an internal radiationless transition, resulting in the accumulation of surface vibration modes (surface heating) and initiating the following surface reaction.[19] On the basis of these results, it is presumed that there are basically two mechanisms for the initiation of the polymerization of DA-LB on the substrates under the illumination at 532 nm: (1) a two-photon or multiphoton processes of DA-LB on the SERS-active substrates to excite the $S_0 \rightarrow S_1$ transition, resulting in the formation of a diradical or a dicarbene of DA as an initial reactive monomer[16,22] and (2) surface heating associated with the 532 nm illumination of DA-LB on the substrates, resulting in the initiation of the thermal polymerization. The facts that a temperature rise due to the surface heating is expected to be at most several degrees[19] and that the polymerization proceeds at low temperatures below -50 °C suggest that the mechanism 1 is more favorable for the initiation of the polymerization of DA-LB on the SERS-active substrates, although the mechanism 2 cannot be totally ruled out. To clarify this point, we need more detailed experiments such as observing the dependence of the reaction rates on the power of excitation laser power.

The propagation process, which follows the initiation, proceeds thermally, the activation energy of the process being 31.6 $\pm$ 9.2 kJ/mol for the ITO substrate and 8.2 $\pm$ 5.4 kJ/mol for the mica substrate. According to Chance and Patel,[14] who studied the thermal polymerization of 2,4-hehadiyne-1,6-diol bis-(p-toluene sulfonate) in the solid state, the polymer conversion

versus time shows a sigmoidal curve displaying an autocatalytic effect, a typical thermal activation energy when interpreted in terms of the time required to reach 50% conversion being reported to be 22.2 ± 0.4 kcal/mol. The thermal activation energy is of the same order as the activation energies of the blue phase formation of the DA-LB films on the ITO and mica substrates, suggesting that the polymerization proceeds similarly in both cases.

The kinetic parameters, k_3 and k_4, for the second process are almost constant in the temperature range of −50 to −70 °C, irrespective of the ITO and mica substrates. Thus, the activation energies for the formation of the red phase and its degradation are almost negligibly small, indicating catalytic effects on the processes at the hot spot on the SERS-active substrates.

Conclusion

The conclusions of the present paper can be summarized as follows:

(1) The Raman microscopic spectra of the DA-LB films on the SERS-active substrates prove that the polymerization of the films to PDA takes place at low temperatures below −50 °C under the illumination of the 532-nm excitation laser light.

(2) The kinetic analyses of the polymerization processes at the temperature range of −50 to −60 °C, based on the SERS spectral changes, indicate that there exist at least two kinds of polymerization processes on the substrates; that is, one of the processes consists of the formation of PDA in the blue phase and its subsequent conversion to the red phase, which is similar to the reaction process of the DA-LB films on solid substrates under illumination of UV-light reported by several authors,[6,9,11] and another one consists of the direct conversion from the DA monomers to the red phase and subsequent degradation.

(3) The spectra were measured by irradiating the sample surface with the excitation laser spot with a diameter of ca. 10 μm. Then, the above-mentioned observation can be explained by considering that the spectral changes monitor the surface reactions occurring at different sites. It was presumed that the formation of the blue phase and its conversion to the red phase take place at a site with relatively low SERS activity, and the direct formation of the red phase and its degradation take place at a site with high SERS activity (or "hot spot").

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