

Surface-Enhanced Photopolymerization of a Diacetylene Derivative in Langmuir–Blodgett Films on a Silver Island Film

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Surface-enhanced resonance Raman scattering (SERRS) spectroscopy was applied to monitor the photopolymerization process of one monolayer ($L = 1$) of a Langmuir–Blodgett (LB) film of the cadmium salt of a diacetylene monocarboxylic acid derivative, 10,12-pentacosadiynoic acid (DA), prepared on an evaporated silver island film with a mass thickness of 60 Å. The result indicated that the polymerization proceeds in a way that is similar to that of the multilayer LB films ($L \geq 3$) of DA prepared on a smooth silver substrate with a mass thickness of 1000 Å, exhibiting a transition from a blue phase ($\lambda_{\text{max}} \approx 635$ nm) to a red phase ($\lambda_{\text{max}} \approx 540$ nm). In addition, the photopolymerization on the SERS-active substrate with $d = 60$ Å was found to proceed much faster than that on the smooth (SERS-inactive) substrate ($d = 1000$ Å). The rate of the photopolymerization of the monolayer on the island film was compared with the rates of a series of LB films of DA prepared on evaporated silver films with $d = 60$ –1000 Å, including the DA Langmuir–Blodgett monolayer sample, into which the spacer layer of LB films of arachidic acid was inserted to control the separation distance between the reacting monolayer and the silver substrate ($d = 60$ Å). On the basis of these results, we proposed that the enhanced photopolymerization is due to an accelerated propagation reaction (an addition reaction of DA to reactive polydiacetylene oligomers) resulting from an enhanced band-to-band transition of the oligomers caused by a strong coupling of the transition to the localized plasmon resonance of the substrates.

Introduction

Surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS) spectroscopies have been established as powerful methods to record surface vibrations of adsorbates on coinage metals such as silver, gold, and copper.^{1–3} In this paper we applied the SERRS and resonance Raman scattering (RRS) spectroscopies to clarify new aspects of UV-irradiation-induced photopolymerization processes of the Langmuir–Blodgett (LB) films of the cadmium salt of a diacetylene carboxylic acid, 10,12-pentacosadiynoic acid (DA), on evaporated silver substrates.

It is a well-known fact that certain substituted diacetylenes forming single crystals and LB films undergo polymerization upon exposure to heat, UV, and γ -ray irradiation.⁴ A unique feature of the reaction in the single crystals is that it proceeds within the crystal lattices, and, being controlled by the packing of the monomers, it leads to perfect single crystals of the corresponding polydiacetylenes. The UV- and γ -irradiation-induced polymerization of the LB films of a long-chain diacetylene monocarboxylic acid such as DA proceeds with retention of the LB assembly, resulting at first in the formation of a deep blue color, which changes into an intense purple-red after passing through a violet phase under continuous irradiation.^{5–11} The color transition can be ascribed to a change in electronic states of a polymer backbone, and the origin of the transition has been studied by using a variety of methods including X-ray diffraction,⁵ UV–vis absorption spectroscopy,^{5–9,11,12} RRS spectroscopy,^{7,10} electron diffraction, and electron microscopy.^{6–9} Mino et al.¹¹ studied the color change of the polymerized LB films of DA by using UV–vis and

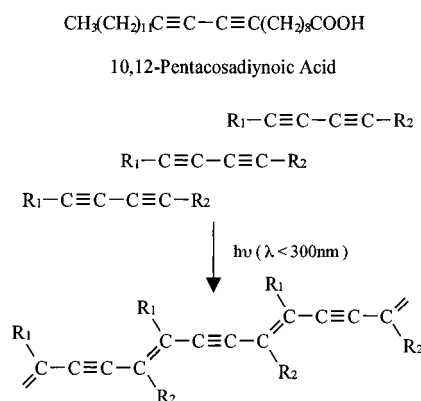


Figure 1. Structure and photopolymerization process of 10,12-pentacosadiynoic acid (DA).

infrared (IR) spectroscopies and differential scanning calorimetry and explained the change as due to an onset of a fluctuation and/or a structural disorder of the side chain groups linked to the polymer backbone. We also used absorption, infrared reflection absorption (IRA), and RRS spectroscopies to delineate conformation changes during the polymerization process of the multilayer LB films (the number of LB films $L \geq 3$) of DA prepared on a flat (or SERS-inactive) silver surface with a mass thickness of 1000 Å.¹³ The results indicated that the polymerization proceeds through two steps, being almost completed in the first step, although a residual reaction may take place in the second step. The blue-phase formation proceeds in the first step, in which the polymer backbone keeps a regular trans zigzag structure and a regular plane formed by the all-trans alkyl chains changes its orientation from a tilted state to a less tilted one. In

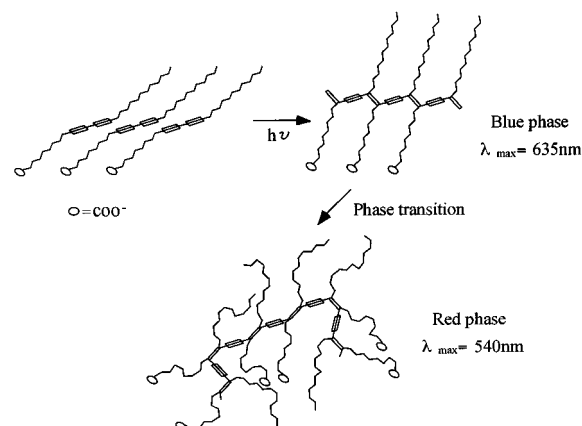


Figure 2. Schematic representation of the photopolymerization processes revealed by the RRS spectroscopy of DA-LB films.

the second step the regular plane of the all-trans alkyl groups is converted to an irregular one containing gauche conformations. The conversion accompanies the shift of a RRS band due to a $\text{C}\equiv\text{C}$ stretching mode of polydiacetylene (PDA) from 2078 to 2101 cm^{-1} , which was interpreted as due to an interruption of the fully extended PDA backbone or to a reduction of the average conjugation length. So as far as the PDA structure monitored by RRS spectroscopy ($\lambda_{\text{ex}} = 514.5$ nm) is concerned, the red phase contains an appreciable amount of irregularity, as schematically shown in Figure 2.¹⁴

To know whether the photopolymerization mechanism of the multilayers can be applied to the case of the polymerization of a one-monolayer LB film of DA, we applied the SERRS and RRS spectroscopies by using silver films with various thickness ($d = 60\text{--}1000$ Å) as substrates. (We used a 532 nm laser line for the excitation source for the spectroscopy. As explained below, polydiacetylene (PDA) obtained from DA gives rise to absorption bands around 540 and 635 nm, which are near the excitation wavelength. In consequence, the SERS bands from PDA are appreciably enhanced by the resonance Raman effect. Although we have not performed any quantitative estimate of the enhancement, we refer to the spectroscopy as SERRS spectroscopy in the present paper.) The results indicated that the substrate with $d = 60$ Å, which is known to form a silver island film, exhibits enough SERS activity to monitor the photopolymerization. In addition, the photopolymerization rate of the monolayer prepared on the island film (hereafter, the sample is abbreviated as DA-LB ($L = 1$)/Ag (60 Å)) was appreciably accelerated compared with that of DA-LB ($L = 5\text{--}15$)/Ag (1000 Å), indicating that the photopolymerization was enhanced on the SERS-active substrate. Theoretical aspects of enhanced photochemistry of molecules adsorbed on SERS-active substrates have been studied in detail by Nitzan and Brus,¹⁶ and experimental evidence for the enhancement has been presented for the photodegradation or photofragmentation processes of dimethyl cadmium,¹⁷ aromatic molecules,^{18,19} and phtharazine.²⁰ Despite these experimental studies, however, it is still unclear whether the enhancement is a general phenomenon or not for the photochemical processes on rough (or SERS-active) silver surfaces. So we performed a series of experiments to clarify the relationship between the photopolymerization rate of the PD-LB films on silver substrates and their SERS activity. On the basis of these results, we proposed a mechanism for the enhanced photopolymerization, giving a new aspect on the photochemistry of the SERS-active substrates.

Experimental Section

Materials. DA was purchased from Wako Pure Chemicals Co. Ltd. and used as received. Arachidic acid and other chemicals were purchased from Kanto Chemicals Co. Ltd. and used without purification. Ag (99.999%) and In (99.99%) were obtained from Kojundo Chemical Laboratory Co. Ltd.

Preparation of LB films. The LB films of DA were prepared by using a Kyowa Kaimen Kagaku, HBM-AP2, Langmuir trough with a Wilhelmy balance. Water used for the preparation was purified with a Millipore water purification system (Milli-Q, four-bowl). A CdCl_2 solution was added to the trough water to a level of 2×10^{-4} mol/L at pH 6.8 (adjusted by NaHCO_3) in order to convert DA and arachidic acid (used as spacer layers) to the corresponding cadmium salts. A monolayer of either DA or arachidic acid in chloroform (2×10^{-3} mol/L) was spread on the trough water by dropwise addition and transferred to a substrate by a vertical dipping method at a surface pressure of 20 mN/m and at 20 °C. The substrates were prepared by a vacuum evaporation of silver on a glass slide. The mass thickness of the silver layers was monitored by a microbalance (ULVAC Japan Ltd., model CRTM-5000). The following abbreviations are used for film samples: DA-LB (L)/Ag (d Å) corresponds to the LB films of DA with the number of monolayers L prepared on the silver substrate with a thickness of d Å, and DA-LB (L)/spacer layer (L')/Ag (d Å) to the LB films having the spacer LB films of cadmium arachidate with a number of layers L' .

Photopolymerization. A 200 W high-pressure mercury lamp (Oriental Lamp model 6283) was used as a UV-irradiation source. A quartz lens ($f = 200$ mm) was used to adjust the intensity of the UV light to be 11 mW/ cm^2 at the surface of each LB film sample.

Absorption Spectral Measurement. Absorption reflection spectra of LB films were measured by using a Unisoku Co. Ltd. rapid-scan spectrometer, model RSP 601, with an incidence angle of about 60°.

RRS Spectral Measurement. RRS and SERRS spectra were measured by using a Kaiser Optical System Holospec ($f/1.8$) spectrometer equipped with a supernotch filter (for 532 nm) and a multichannel detector (Princeton Instruments Inc., ICCD-576G/B). The 532 nm line from a CW Nd:YAG laser (Spectron Laser Systems, model DTL-116A) was used as an excitation source. The following precautions were taken to eliminate polymerization during RRS and SERRS measurements: (i) The laser power was as small as possible (<2 mW). (ii) A rotating sample method was employed. (iii) The accumulation time for RRS measurements was as short as possible (less than 1 min).

Results and Discussion

Photopolymerization Process of DA-LB ($L = 15$)/Ag (1000 Å). The RRS spectral changes of DA-LB ($L = 15$)/Ag (1000 Å) during the UV-irradiation-induced polymerization were already reported in a previous studies (Figure 9 of ref 12 and ref 13). For comparison purposes, we remeasured the spectral change under the same irradiation conditions employed by the present study. The results are shown in Figure 3, the S/N ratios of which are much better than those of the previous spectra. This is due to the spectrometer ($f/1.8$), which is much more efficient than that ($f/6.4$) used by the previous study. The RRS bands near 2100 cm^{-1} are due to a $\text{C}\equiv\text{C}$ stretching vibration of a polydiacetylene (PDA), and those near 1480 cm^{-1} are due to a $\text{C}=\text{C}$ stretching vibration overlapped by a CH_2 scissoring vibration at 1452 cm^{-1} .²¹ The $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})$ bands appear at 2084 and 1478 cm^{-1} , respectively, at the beginning

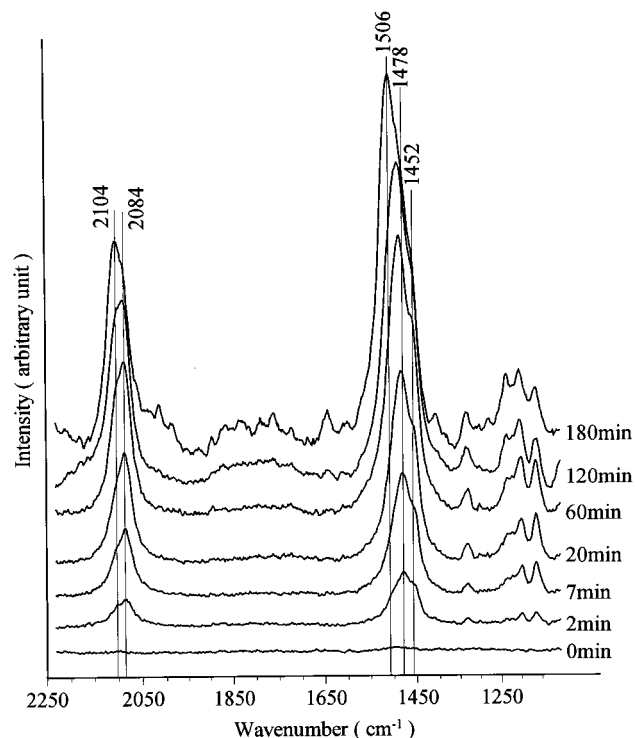


Figure 3. RRS spectral changes during the photopolymerization of DA-LB ($L = 15$)/Ag (1000 Å). The irradiation time is indicated on the right-hand side of each spectrum. $\lambda_{\text{ex}} = 532$ nm.

of the UV irradiation and shift to 2104 and 1506 cm^{-1} , respectively, as the polymerization proceeds. As already explained, these shifts indicate that the blue-to-red phase transition of PDA accompanies a partial conversion of the PDA backbone to an irregular structure.¹³ Following the procedure of the previous paper,¹³ we performed the curve resolution of the $\nu(\text{C}\equiv\text{C})$ bands around 2100 cm^{-1} under the assumption that the bands are composed of three Lorentzian components at 2083, 2095, and 2111 cm^{-1} . The 2083 cm^{-1} band is due to the blue phase and the 2111 cm^{-1} band due to the irregular part of the PDA backbone in the red phase. The 2095 cm^{-1} component was assumed because we could not obtain good fits between the observed and calculated spectra with only the blue and red phase components. The intermediate frequency of the 2095 cm^{-1} component suggests that the component is ascribable to PDA with an intermediate conjugation length.^{13,22} It is, however, not clear whether the component is ascribable to PDA oligomers or to an intermediate state of the blue-to-red phase transition. The part of PDA associated with the component does not participate in the blue-to-red transition, as explained below. Figure 4 plots the relative intensities of the three component bands as a function of irradiation time. As can be seen from the figure, the intensity of the 2083 cm^{-1} (blue phase) band shows a precipitous increase with the onset of irradiation, maximizes after about 40 min of irradiation, and then decreases. On the other hand, the intensity of the 2111 cm^{-1} band (red phase) shows a gradual increase at the initial stage of polymerization, and after about 40 min it begins to increase at an accelerated rate. These results indicate that the formation of the blue phase in DA-LB ($L = 15$)/Ag (1000 Å) is almost completed during the irradiation of 40 min and after that there occurs the conversion from the blue phase to the red phase. The intensity of the third component increases at a rate between those of the blue and red phases, and after about 80 min it becomes almost constant. Thus, the intensity change of the third component does not correlate with those of the other compo-

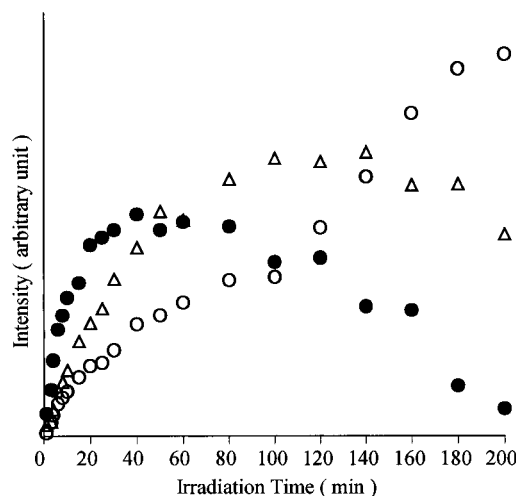


Figure 4. Relative intensity changes of the component bands as a function of irradiation time observed for the RRS spectra during the photopolymerization of DA-LB ($L = 15$)/Ag (1000 Å): (●) 2083 cm^{-1} ; (○) 2111 cm^{-1} ; (△) 2095 cm^{-1} . See text.

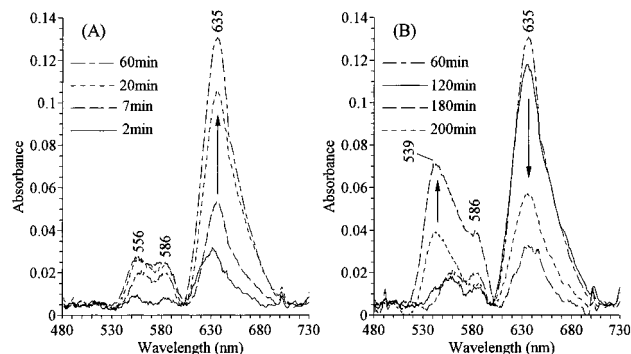


Figure 5. Absorption spectral changes during the photopolymerization of DA-LB ($L = 15$)/Ag (1000 Å): (A) irradiation time of 2–60 min; (B) irradiation time of 60–200 min.

nents, suggesting that the PDA oligomers associated with the third component do not participate in the blue-to-red phase transition.

Figure 5 illustrates the absorption spectra observed for DA-LB ($L = 15$)/Ag (1000 Å) during the photopolymerization. The spectral changes are similar to those already observed.^{9,13} The intensity of the band at 635 nm ascribable to the blue phase increases from the beginning, maximizes at about 40–60 min, and then decreases. On the other hand, the 539 nm band due to the red phase appears at about 60 min and then increases its intensity and dominates the spectrum at 200 min. These results conform to the relative intensity change of the $\nu(\text{C}\equiv\text{C})$ bands due to the blue-to-red transition. The figure gives the bands near 556 and 586 nm, the intensities of which increase at an initial stage of polymerization and stay almost constant after about 60 min. These bands may be ascribed to a part of the PDA backbone associated with the $\nu(\text{C}\equiv\text{C})$ band at 2095 cm^{-1} .

Photopolymerization Process of DA-LB ($L = 1$)/Ag (60 Å). The SERRS spectral changes observed for DA-LB ($L = 1$)/Ag (60 Å) as a function of UV irradiation time are summarized in Figure 6 together with the RRS spectrum of DA-LB ($L = 1$)/Ag (1000 Å) measured after irradiation for 10 min (bottom spectrum). As can be seen from the figure, DA-LB ($L = 1$)/Ag (60 Å) exhibits spectral changes for the $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})$ bands similar to those in Figure 3, indicating that the monolayer undergoes photopolymerization. As the polymerization proceeds, the $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})$ bands show frequency

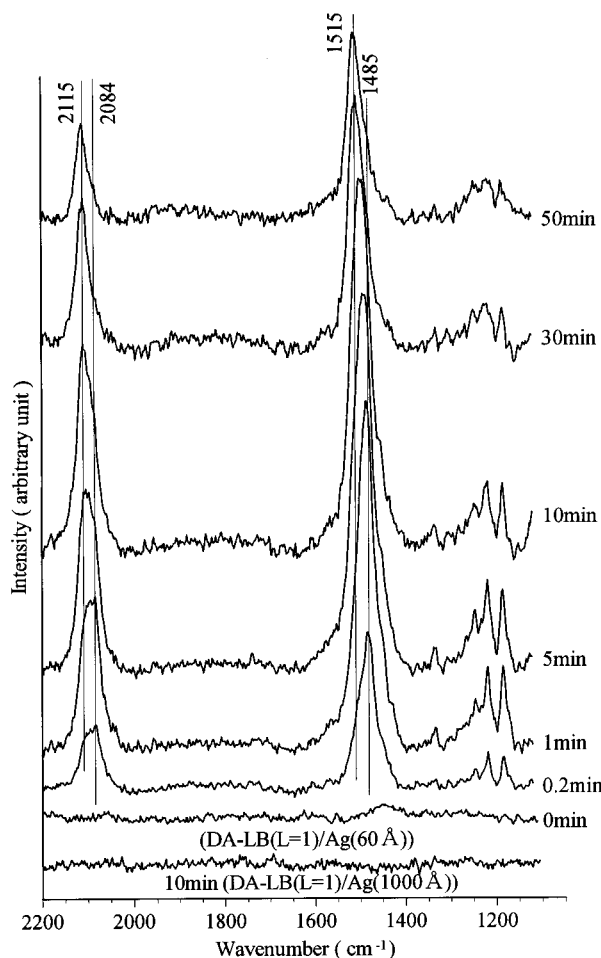


Figure 6. Comparison of the RRS spectrum (bottom) measured for DA-LB ($L = 1$)/Ag (1000 Å) after irradiation for 10 min and the SERRS spectra measured for DA-LB ($L = 1$)/Ag (60 Å) after irradiation for 0–50 min. $\lambda_{\text{ex}} = 532$ nm.

shifts of $2084 \rightarrow 2115 \text{ cm}^{-1}$ and $1485 \rightarrow 1515 \text{ cm}^{-1}$, respectively, indicating the blue-to-red phase transition. On the other hand, the spectrum of DA-LB ($L = 1$)/Ag (1000 Å) measured after 10 min of irradiation does not show any detectable change. This result proves that, in contrast to the case of the polymerization on the silver substrate with $d = 60$ Å, the film on the substrate with $d = 1000$ Å does not undergo a detectable photopolymerization. (The RRS spectral changes due to UV irradiation of DA-LB ($L = 1$)/Ag (1000 Å) observed by using a liquid-nitrogen-cooled CCD detector, which is much more sensitive than the ICCD detector employed in the present study, however, indicated that after prolonged irradiation the film does give a weak but sharp band at 2099 cm^{-1} ascribable to the $\nu(\text{C}\equiv\text{C})$ band of PDA. This peak does not show any frequency shift, in contrast to the cases of DA-LB ($L = 15$)/Ag (1000 Å) (Figure 3) and DA-LB ($L = 1$)/Ag (60 Å) (Figure 6). We tentatively assigned this band to a PDA oligomer, which is terminated at an embryonic stage of polymerization.) The curve resolution was performed on the $\nu(\text{C}\equiv\text{C})$ bands in Figure 6 under the assumption of 2083 (blue phase), 2103, and 2115 cm^{-1} (red phase) components. Figure 7 illustrates the results of the procedure, which reproduce the observed spectra quite well, proving the validity of the assumption. Figure 8 plots the relative intensities of the component bands as a function of irradiation time. As can be seen from the figure, the intensity of the $\nu(\text{C}\equiv\text{C})$ band due to the blue phase at first increases precipitously, maximizes at about 2.5 min, and then decreases, while the intensity of the $\nu(\text{C}\equiv\text{C})$ band due to the red phase

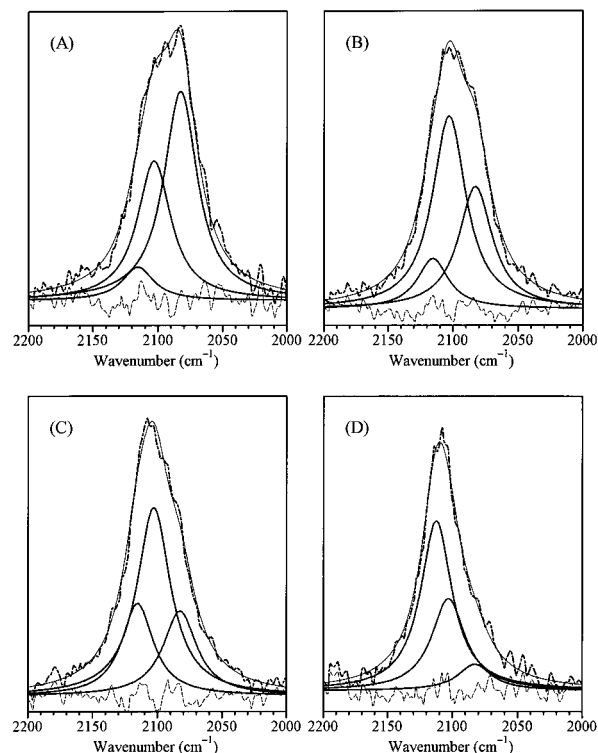


Figure 7. Results of the curve resolution procedure performed on the SERRS spectra shown in Figure 6 measured at irradiation time of 0.2 (A), 5 (B), 10 (C), and 40 (D) min. Dash-dotted, thin solid, and thick solid curves denote observed, calculated, and component spectra, respectively. Dashed lines express the difference between the observed and calculated spectra (see text).

continues to increase after 2.5 min. This result confirms that DA-LB ($L = 1$)/Ag (60 Å) exhibits the blue-to-red phase transition similar to that observed for DA-LB ($L = 15$)/Ag (1000 Å). Comparing the plots in Figure 8 with those in Figure 4, however, we notice explicit differences. That is, the completion of the blue-phase formation takes place much faster on the substrate with $d = 60$ Å than on the substrate with $d = 1000$ Å. (We measured the RRS spectral changes induced by UV irradiation for DA-LB ($L = 5$)/Ag (1000 Å). The relative intensity changes of the component bands due to $\nu(\text{C}\equiv\text{C})$ are almost identical with those in Figure 4. We cannot explain the faster transition observed for DA-LB ($L = 1$)/Ag (60 Å) as due to the smaller number of the LB layers.) In addition, Figure 8 indicates that after about 20 min of irradiation all the component bands begin to reduce their relative intensities, which was not observed for the photopolymerization of DA-LB ($L = 15$)/Ag (1000 Å). The result may be ascribed to an enhanced photodegradation of PDA and PDA oligomers.

Before examining the reasons for the enhanced photopolymerization on the substrate with $d = 60$ Å, we performed several experiments to confirm the SERRS activity of the substrate with $d = 60$ Å. First, we measured the SERRS and RRS spectra of PDA on silver films with a thickness of 60–1000 Å. PDA was prepared by UV irradiation of a DA monolayer spread on the trough water (at 20 mN/m and 20 °C). One monolayer of PDA was transferred to each substrate by a vertical dipping method. Table 1 summarizes the relative intensities of the $\nu(\text{C}\equiv\text{C})$ band, indicating that (i) the substrate with $d = 60$ Å gives the strongest relative intensity and (ii) the larger the effective thickness, the smaller the relative intensity. The substrate with $d = 60$ Å is considered to form an island film, and the results can be explained by considering that as the thickness increases, the silver islands on the substrates coalesce

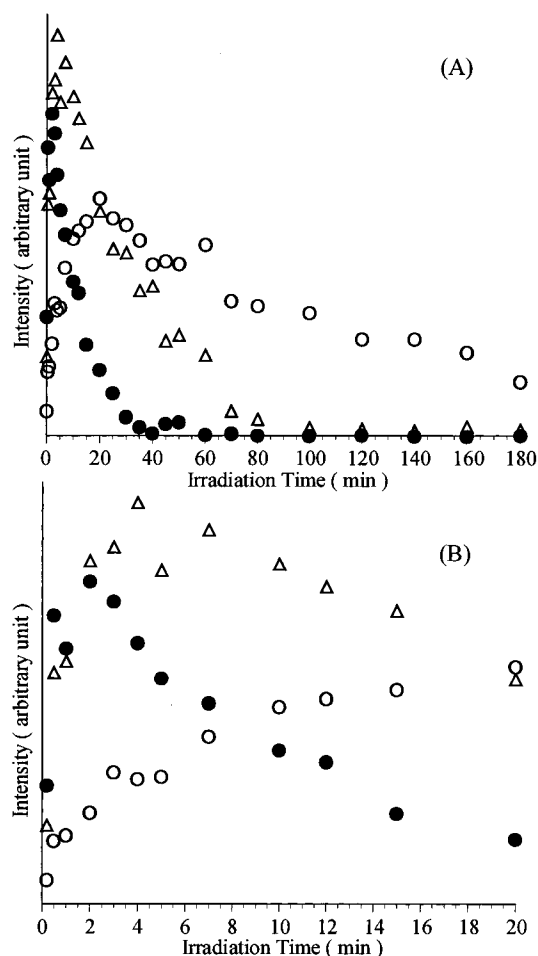


Figure 8. Relative intensity changes of the component bands as a function of irradiation time (A, 0–180 min; B, 0–20 min) observed for the SERS spectra during the photopolymerization of DA-LB ($L = 1$)/Ag (60 Å): (●) 2083 cm^{-1} ; (○) 2115 cm^{-1} ; (△) 2103 cm^{-1} . See text.

TABLE 1: Relative Intensities of the $\nu(\text{C}\equiv\text{C})$ Band of an LB Monolayer of PDA Prepared on Ag Substrates with Various Mass Thicknesses (See Text)

thickness (Å)	relative intensity	thickness (Å)	relative intensity
60	286	250	10
120	87	1000	1
180	14		

TABLE 2: Relative Intensities of the $\nu(\text{C}\equiv\text{C})$ Band of an LB Monolayer of PDA Prepared on a Ag Substrate with a Thickness of 60 Å Containing Spacer Layers (LB Films of Cadmium Arachidate) with Various Thickness between the Monolayer and the Substrate (See Text)

no. of spacer layers	relative intensity	no. of spacer layers	relative intensity
0	286	3	56
1	63	5	55

with each other, causing the formation of less efficient surface morphology for the SERS effect. Second, we measured the relative intensity of the $\nu(\text{C}\equiv\text{C})$ band of the PDA monolayer prepared on top of the spacer LB films of cadmium arachidate ($L' = 1-5$) on the silver substrate with $d = 60$ Å. The results are summarized in Table 2, which indicates that as the number of spacer layers increases, the relative intensity decreases. This is again a characteristic feature of the SERS effect.²³ Thus,

the result in Table 2 also confirms the SERS activity of the silver substrate with $d = 60$ Å.

As explained above, the monolayer DA-LB undergoes photopolymerization as well as the blue-to-red phase transition on the SERS-active substrate, while the monolayer on the flat (or SERS-inactive) substrate exhibits neither detectable polymerization nor the blue-to-red phase transition. In addition, if we take the time at which the relative intensity of the blue-phase $\nu(\text{C}\equiv\text{C})$ band maximizes as an estimate of the polymerization rate, the monolayer on the SERS-active substrate proceeds much faster than DA-LB ($L = 15$)/Ag (1000 Å). Although the spectra of PDA observed for DA-LB ($L = 1$)/Ag (60 Å) in Figure 6 are enhanced by the SERS effect, this cannot be considered as the reason for the enhanced rate because if the polymerization proceeded at the same rate as that for DA-LB ($L = 1$)/Ag (1000 Å), the spectral changes in Figure 6 would be observed for the latter sample by using the more sensitive detector, which is not the case, as mentioned in the previous section.

Possible Reasons for the Enhanced Photopolymerization Rate of DA-LB ($L = 1$) on the SERS-Active Ag Film ($d = 60$ Å). It has been proposed that the photopolymerization of diacetylene derivatives in solid states consists of the following steps: (i) an $S_0 \rightarrow S_1$ transition ($\lambda < 300$ nm) of a monomer molecule, resulting in the formation of reaction centers including a reactive diradical and/or dicarbene oligomers; (ii) a photoinduced chain propagation reaction (addition of monomer molecules to the reaction centers); (iii) a chain termination reaction.²⁴ Bubeck et al.²⁵ studied the photopolymerization reaction of a multilayered LB films of DA ($L = 40$) prepared on a quartz plate and reported that whereas the first step is initiated by UV irradiation only, irradiation of the partially polymerized layer with visible light up to $\lambda \leq 500$ nm leads to the continuation of the reaction (the second step). The action spectrum of the second step (the dependence of the reaction rate on the wavelength of irradiation) does not correspond to the polymer absorption spectra in Figure 5. However, it corresponds very well to the photocurrent action spectrum of fully polymerized diacetylene multilayers reported by Lochner et al.,²⁶ giving evidence that the oligomer band-to-band transition is involved in the chain propagation process. On the basis of these results, Bubeck et al.²⁵ concluded that free charge carriers excited by light through the band-to-band transition can easily move along the reactive oligomers and subsequently activate the chain end group, which enables the addition of adjacent monomer units and thus initiates the chain propagation. According to Bubeck et al.,²⁵ the activation does not necessarily need to be a charge-transfer process to the adjacent monomer unit. It can also be considered in terms of vibrational energy created by the recombination of the charge carriers at the chain unit. Thus, especially in the second step a thermal process induced by a deactivation energy of a photoexcited state may play an important role in the addition to a photochemical process.

Several reasons can be considered for the enhanced photopolymerization observed for PD-LB($L = 1$)/Ag(60 Å). (a) As already explained, theoretical as well as experimental evidence has been accumulated for enhanced photochemical processes on rough (or SERS-active) silver surfaces.¹⁶⁻²⁰ The enhancement has been attributed mainly to enhanced molecular absorption processes at rough silver surfaces, which is caused by resonant interaction between absorbing molecules and a strong electric field produced at the surfaces through localized plasmon resonance excited by an incident optical electric field in the

wavelength region longer than about 400 nm. Then the enhanced photopolymerization may be ascribed to the enhanced band-to-band transition through the resonance interaction with the localized plasmon. (b) As mentioned above, a thermal process plays an important role in the propagation reaction. The SERS-active island silver film has a lower thermal conductivity than the SERS-inactive smooth silver film. Then the thermal energy produced by the recombination process may be transferred to the reacting monomer at the island film more efficiently than at the smooth surface, resulting in the enhancement of the photopolymerization. (c) In the case of photochemical reactions at metal surfaces, energy dissipation may compete successfully against the enhanced absorption, thus reducing the photochemical efficiency.¹⁶ It may be possible that this energy-damping process is much more efficient for the reaction process of DA-LB ($L = 1$)/Ag (1000 Å) compared with that of DA-LB ($L = 1$)/Ag (60 Å), thus explaining the enhanced rate of the latter monolayer. (d) Stacking modes and flexibility or mobility of the DA monomers in the LB films may play important roles in the photopolymerization; i.e., an unfavorable stacking and/or a too rigid packing state of the monomers will reduce the photopolymerization rate. These states are determined by several factors including (i) surface morphology of the substrates, (ii) interactions such as an electrostatic interaction between the carboxylate group of DA and the silver substrates, and (iii) the number of the LB layers (DA-LB or spacer LB layers, vide infra), which exist between the reacting LB films and the substrates. Factor iii may affect the flexibility or mobility of the DA monomer; i.e., the larger the number of intervening LB layers, the larger the flexibility of the monomers, thus increasing the polymerization rate.

To determine the most important reason (or reasons) among those cited above (i.e., (a) an enhanced band-to-band transition effect, (b) a thermal effect, (c) a reduced energy dissipation effect, or (d) stacking and/or flexibility effect), we performed the following experiments.

Photopolymerization of DA-LB ($L = 1$)/Ag ($d=60\text{--}250$ Å) and DA-LB ($L = 1$)/Spacer LB ($L' = 0\text{--}3$)/Ag (60 Å). To confirm the correlation between the SERS activity of silver substrates and the photopolymerization rate, we measured the spectral changes during the photopolymerization of DA-LB ($L = 1$) prepared on silver substrates with thickness of 60–250 Å. Figure 9 illustrates the spectra measured after irradiation for 30 min. The spectrum measured for DA-LB ($L = 1$)/Ag ($d = 60$ Å) gives the bands at 2115 and 1510 cm^{-1} , indicating that the blue-to-red phase transition is completed, while the spectra of DA-LB ($L = 1$)/Ag ($d = 120\text{--}250$ Å) still give the bands at 2104 and 1495 cm^{-1} , indicating that the transition is not completed. Then the polymerization proceeds at the largest rate in the LB films at the substrate with $d = 60$ Å. This can be more clearly seen by plotting the relative intensities of the $\nu(\text{C}\equiv\text{C})$ band associated with the blue phase as a function of irradiation time (Figure 10). The times, at which the intensity of the blue phase $\nu(\text{C}\equiv\text{C})$ maximizes in Figure 10, are as follows: 2.5 min (60 Å), 4 min (120 Å), 4.5 min (200 Å), and 7 min (250 Å). Thus, there is a good correlation between the SERS activity summarized in Table 1 and the rate of polymerization.

Figure 11 compares the SERRS spectra measured after irradiation of 30 min for DA-LB ($L = 1$) on a Ag (60 Å) substrate having spacer layers of the cadmium arachidate with $L' = 1$ and 3. For comparison purposes, the corresponding SERRS spectrum measured for DA-LB ($L = 1$)/Ag (60 Å) is also shown in the figure. The spectrum observed for the sample

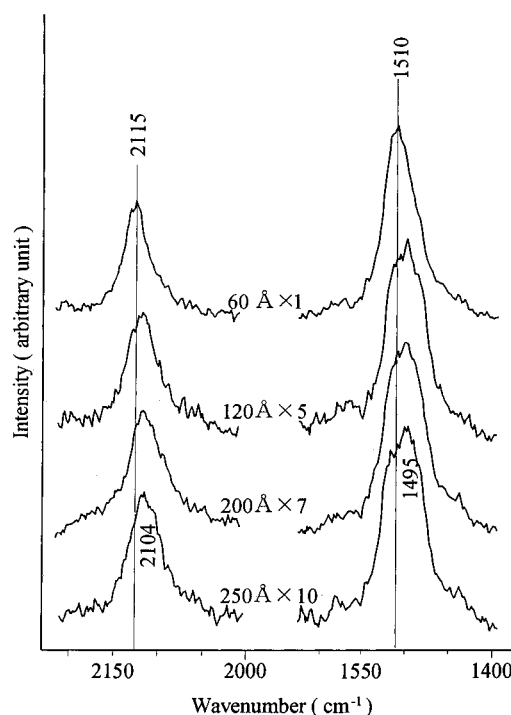


Figure 9. Comparison of the SERRS spectra measured after 30 min of irradiation of DA-LB ($L = 1$) on the Ag substrates with various thickness (60–250 Å). $\lambda_{\text{ex}} = 532$ nm. The thickness is indicated in the middle of each spectrum. Intensity of each spectrum was multiplied by a number indicated in the figure for comparison purposes.

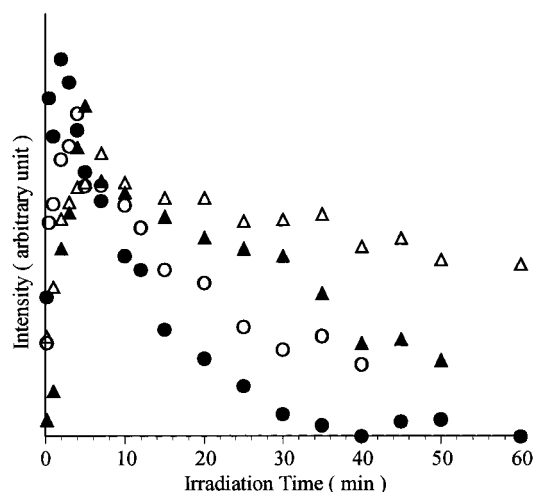


Figure 10. Relative intensity changes of the $\nu(\text{C}\equiv\text{C})$ component associated with the blue phase as a function of the irradiation time observed for DA-LB ($L = 1$)/Ag ($d = 60\text{--}250$ Å). Intensities observed for each substrate were multiplied by a number as shown in Figure 9. Thicknesses of the Ag layer are (●) $d = 60$ Å, (○) $d = 120$ Å, (▲) $d = 200$ Å, and (△) $d = 250$ Å.

film without the spacer layer gives the $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})$ frequencies (2109 and 1510 cm^{-1}) ascribable to the red phase, while the spectrum for the film with the spacer layer ($L' = 3$) still gives the frequencies (2084 and 1483 cm^{-1}) characteristic of the blue phase. The frequencies observed for the film without the spacer layer ($L' = 1$) are between those of the film without the spacer layer and those of the film with the spacer layer ($L' = 3$). Figure 12 plots the relative intensities of the $\nu(\text{C}\equiv\text{C})$ component due to the blue phase in Figure 11 as a function of irradiation time. The plots indicate that the rate of polymerization decreases as the number of spacer layers increases. This

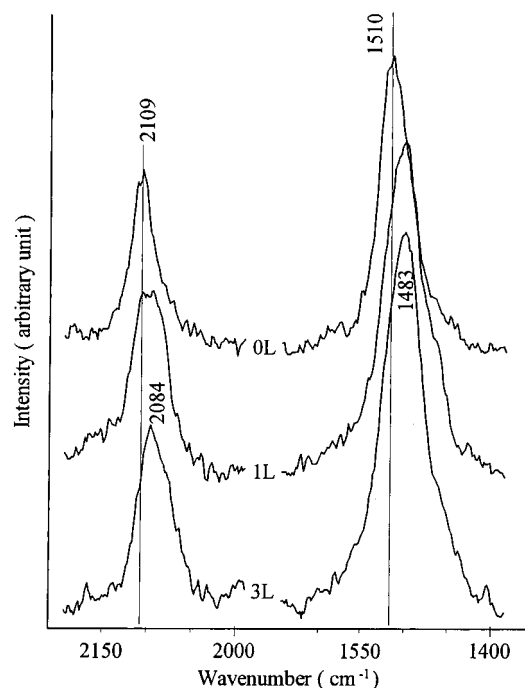


Figure 11. Comparison of the SERRS spectra measured after 30 min of irradiation of DA-LB ($L = 1$)/spacer LB ($L' = 0-3$)/Ag (60 Å). $\lambda_{\text{ex}} = 532$ nm. The number of the spacer layers is indicated in the middle of each spectrum.

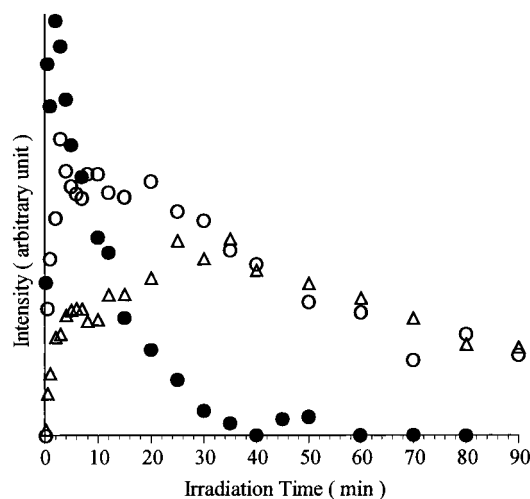


Figure 12. Relative intensity changes of the $\nu(\text{C}\equiv\text{C})$ component associated with the blue phase as a function of the irradiation time observed for DA-LB ($L = 1$)/spacer LB ($L' = 0-3$)/Ag (60 Å). The numbers of spacer layers are (●) $L' = 0$, (○) $L' = 1$, and (△) $L' = 3$.

result again proves the correlation between the rate of polymerization and the SERS activity summarized in Table 2.

Photopolymerization of DA-LB ($L = 5$)/Spacer LB ($L' = 1-11$)/Ag (1000 Å). Although the results explained in the previous section prove to be a good correlation between the rate of the photopolymerization and the SERS activity of the substrates, it does not necessarily mean that the reason a and/or reason b is the only explanation for the enhanced polymerization. To know the effect of the distance between the reacting LB films and the substrate and that of the stacking and mobility of the DA monomers on the polymerization rate, we measured the RRS spectral changes of DA-LB ($L = 5$) prepared on top of the spacer LB films with $L' = 1-11$ on a flat silver substrate ($d = 1000$ Å). The plots of the relative intensity of the blue phase component of the $\nu(\text{C}\equiv\text{C})$ band against irradiation time

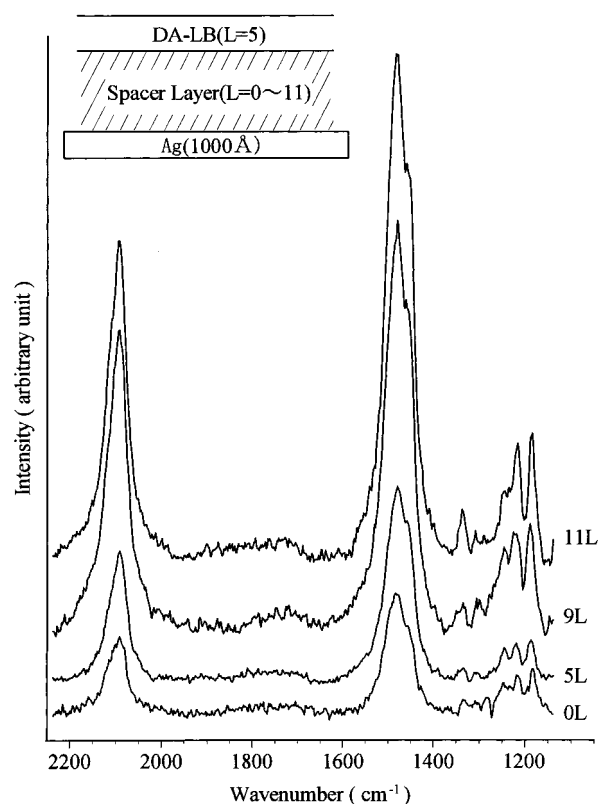


Figure 13. Comparison of the RRS spectra of DA-LB ($L = 5$)/spacer LB ($L' = 1-11$)/Ag (1000 Å) measured after UV irradiation of 20 min. $\lambda_{\text{ex}} = 532$ nm. The number of the LB layers is indicated on the right-hand side of each spectrum.

for all the samples (not shown in the present paper) are virtually identical with those shown in Figure 4, indicating that the polymerization proceeds almost at the same rate in all the samples. This is consistent with the fact that, as shown in Figure 13, the spectral features measured after 20 min of irradiation are almost identical with one another. The intensities of the $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})$ bands, however, increase with the number of spacer layers, indicating that the conversion of the polymerization increases with the number of spacer layers. This result can be explained by either or both of the following two factors: (i) as the thickness of the spacer layers increases, the energy-transfer efficiency decreases, causing an increase in the conversion of the polymerization; (ii) as the thickness increases, the flexibility or mobility of the DA monomers of the LB film increases, which may cause an increase in the conversion. In the case of the polymerization on the SERS-active substrate ($d = 60$ Å), the rate of polymerization decreases as the thickness of the spacer layers increases, as can be seen from Figures 11 and 12. This is contrasted with the case of polymerization on the SERS-inactive substrate (Figure 13). So the difference between the photopolymerization rate on the SERS-active substrate and that on the SERS-inactive one can be ascribed neither to the energy-transfer effect (reason c) nor to the flexibility or mobility effect.

Photopolymerization of DA-LB ($L = 5$)/In (100 Å). The roughness of the SERS-active substrate ($d = 60$ Å) may affect the stacking mode of the monomers in DA-LB ($L = 1$), causing a larger rate of polymerization compared with that on a flat silver substrate ($d = 1000$ Å). To check this possibility, we measured the RRS spectral changes induced by UV irradiation for DA-LB ($L = 5$) prepared on evaporated indium substrates with mass thicknesses of 100 and 200 Å. The surface of these films is known to form an island film similar to that of the

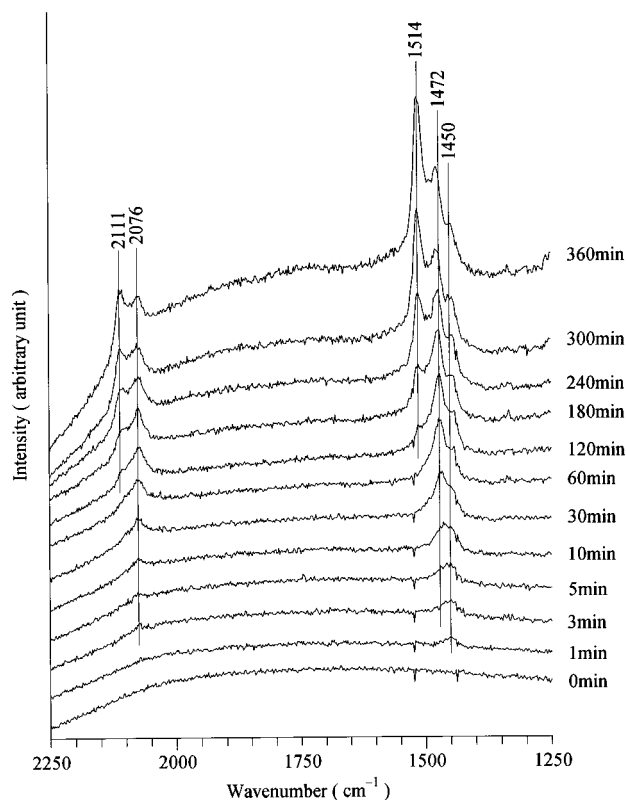


Figure 14. RRS spectral changes during the photopolymerization of DA-LB ($L = 5$)/In (100 Å). The irradiation time is indicated on the right-hand side of each spectrum. $\lambda_{\text{ex}} = 532$ nm.

silver island film.²³ Figure 14 exhibits the spectral changes observed for DA-LB ($L = 5$)/In (100 Å). The RRS bands due to $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})$ show frequency shifts of $2076 \rightarrow 2111$ cm^{-1} and $1472 \rightarrow 1514$ cm^{-1} , respectively, indicating the blue-to-red phase conversion. Comparison of the spectral changes in Figure 14 with those in Figure 3 proves that the photopolymerization rate on the indium substrate is much reduced compared with that on the smooth silver substrate. Thus, the stacking or flexibility effects associated with the surface morphology (or the roughness) is not the main factor for the difference in the polymerization rate between the SERS-active and SERS-inactive substrates. This result, together with that in Figure 13, indicates that reason d cannot be considered as a main reason for the enhanced photopolymerization. In addition, the thermal conductivity of the indium substrate is lower than that of the silver substrates. Then the reduced polymerization rate observed for the indium substrate compared with those for the smooth and SERS-active silver substrates indicates that reason b is not important for the enhanced photopolymerization.

Conclusion

The SERRS spectral changes observed for DA-LB ($L = 1$)/Ag (60 Å) proved that the monolayer undergoes a photopolymerization reaction exhibiting a blue-to-red phase transition, as in the case of the multilayer LB films of DA ($L \geq 3$). As far as the transition mechanism revealed by the SERRS and RRS spectroscopies is concerned, it is a two-dimensional phenomenon by nature and may be explained in the following manner. The photopolymerization induces a repulsive interac-

tion between the repeating units within the monolayer, and when the lateral interaction is accumulated to a certain extent during the blue-phase formation, the layer no longer keeps the ordered structure and begins to relax the accumulated energy by changing into a disordered structure, resulting in the formation of the red phase.

In addition, all the experimental results confirmed that the enhanced photopolymerization is ascribable to reason a. That is, the enhancement can be explained in terms of an enhanced self-sensitization effect of a propagation reaction (i.e., addition reactions of DA monomers to reactive PDA oligomers), which is caused by an intensified band-to-band transition of the reactive oligomers through a strong coupling with the localized plasmon excitation. To more conclusive evidence for the enhancement mechanism, however, we should confirm the correspondence between the localized plasmon band and the action spectrum of the propagation reaction, which is under way in our laboratory.

References and Notes

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- (14) The structure shown in Figure 2 does not conform to the results of the X-ray and electron diffraction studies,^{6,8} which indicated the existence of a layered structure with a smectic order in the red phase. Although RRS spectroscopy provides detailed information about the structure of PDA, the light absorption leads to a large enhancement of the RRS bands of backbone vibrations. Since an irregular structure of PDA backbones exhibits an absorption band near 500 nm,¹⁵ the RRS band at 2101 cm^{-1} ascribable to the irregular part may be selectively enhanced by the excitation at 514.5 nm, even if the content of the part is small. This may explain the discrepancy between the model in Figure 2 and that proposed by the X-ray and electron diffraction studies.
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