Cooperative photoinduced two-dimensional condensation in Langmuir films observed using nanosecond pump-probe Brewster angle microscopy

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Two-dimensional condensation was initiated in a self-assembled mixed monolayer of spiropyran and octadecanol by a nanosecond laser pulse. The dynamics of the process were monitored using nanosecond pump-probe Brewster angle microscopy. Domain growth followed a power law with a growth exponent of 0.47 at a velocity approaching 20 ms^{-1}. This represents a limit for the rate of longitudinal signaling of pressure waves through a self-assembled amphiphilic layer at an interface and adds to our understanding of signal transmission rates in biomimetic membranes where morphological change in one region can be signaled to a more remote region. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3507241]

I. INTRODUCTION

Phase domain growth in two dimensions has been the subject of many theoretical studies.[1–5] However, real phase-changing systems are nearly always three-dimensional,[6–16] or at least could be argued to have a significant component from a third dimension.[17,18] Langmuir films are molecular monolayers at an air-liquid interface that do provide a system approaching two dimensions in that they are a two-dimensional arrangement of molecules layered upon a bulk subphase that gives the system an added dimension that is reasonably unaffected by changes in the monolayer. Hence, the system is effectively two-dimensional. Additionally, they are of interest in their own right since they are models for biological self-assembled membranes.
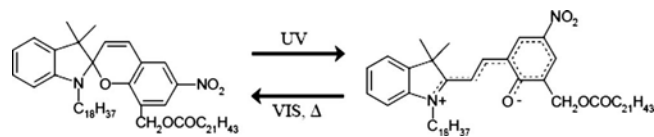
Spiropyran (SP) having two long alkyl chains as shown in Scheme 1 can form homogeneous monolayers when mixed with octadecanol (OD) in a ratio of 1:2. SP can photochemically convert to metastable photomerocyanines (PMCs) by undergoing a molecular rearrangement that makes the alkyl chains change from being orthogonal to in-plane. This means that partially converting from SP to PMC will change the surface pressure isotherm of the monolayer so that it is possible to induce a phase transition from a gaslike state to a gas-liquid coexistence state at ~2 nm^2/molecule of SP.[19–22] In the current work, a nanosecond pulsed laser was used to rapidly bring about this transition by jumping the system from one isotherm to another. We have previously described this phenomenon in pure SP monolayers;[23] however, detailed analysis of domain growth was compromised by the fact that the starting monolayer of pure SP was already inhomogeneous.

II. EXPERIMENT

The apparatus used in this study has been described previously.[23–25] Briefly, a 355 nm, 5 ns pulse from a neodymium-doped yttrium aluminum garnet (Nd-YAG) laser (Spectra Physics CGR230, 8 ns, 24–100 mJ/pulse cm^{-2}) is made incident at 90° to a liquid surface overlaid with a SP monolayer. This initiates photoinduced effects at the interface. This pump laser is synchronized with a second Nd-YAG probe laser (Quantel Brilliant, 532 nm, 8 ns, highly *p*-polarized) using a delay generator (Stanford Research Instruments SRI DG535). The probe laser is incident to the monolayer at the Brewster angle of the air-water interface. Images are collected using a charge coupled device camera that is also synchronized to the arrival of the probe pulse and positioned to collect light reflected at the Brewster angle. In this way, time-resolved images of phase domains in monolayers can be imaged as they evolve after laser excitation. The apparatus has nanosecond time resolution as limited by the laser pulse duration.

Pressure isotherms for this system were determined for pure SP monolayers, as well as for SP-OD monolayers in a 1:2 molar composition, in a Langmuir trough with a Wilhelmy balance, to establish the expected UV-laser induced change in the monolayer; continuous UV irradiation was used to excite the monolayer to a photostationary mixture and the pressure isotherm was remeasured. From these data, the initial surface coverages were selected (2 nm^2/SP molecule in the OD-SP). This coverage was selected because, based on the isotherms with and without irradiation, we could expect that the monolayer would jump from gaslike monolayer to a gas-liquid coexistence-type monolayer upon partial photoconversion to the PMC form.

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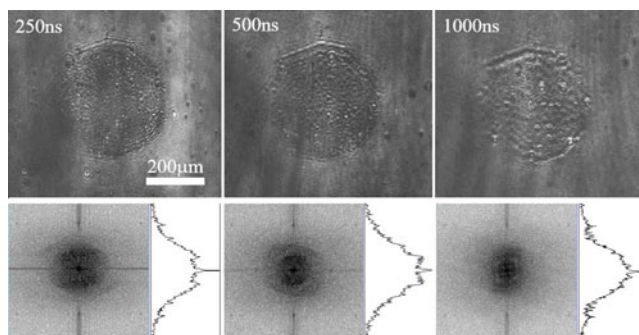
SCHEME 1. Spiropyran-photomerocyanine system.

FIG. 2. Time resolved BAM images for the evolution of the wave pattern in the 1:2 OD-SP monolayers after pulsed laser irradiation at a fluence of 24 mJ/pulse cm^{-2} with the corresponding Fourier transforms and intensity profiles shown below.

III. RESULTS AND DISCUSSION

The Langmuir isotherms used to select the initial conditions for the SP systems used are shown in Fig. 1. As can be seen, the expected pressure jump in the pure SP monolayer is larger than in the SP-OD monolayer; however, since the starting condition for the pure monolayer was already inhomogeneous, the SP-OD mixed monolayer was selected for further kinetic analysis.

The kinetics of the photochemical conversion to the ring open form in the presence of oxygen is expected to be rapid and would occur over timescales of the order of less than 100 ns, meaning that the system's final composition is achieved within this time.[26]

From the time-resolved Brewster angle microscope (BAM) images, we could see that after photoexcitation with a pulsed laser, the monolayer evolved and a "wave"-type structure appeared in the irradiated region. The typical time evolution of the wave-type pattern in such a monolayer is shown in Fig. 2. The wave structure became obvious by 100

ns following photoexcitation and its wavelength grew with time until it became indiscernible from the nonirradiated region at around 10 μs. From the Fourier transforms of these images, it could be seen that there were weak maxima in the power spectra, indicating that the wave structure had a characteristic length scale. The growth of the wavelength with time is shown in Fig. 3. The initial growth of the wavelength could be described by the power law $L=(0.32)t^{0.47}$. However, after 1 μs, the growth expression changed to $L=(3.6)t^{0.12}$.

Possible causes of the wave pattern other than the expected one, based on the experimental design, will be ruled out one by one. These being either temperature gradients leading to density fluctuation or demixing of the SP and PMC.

First, temperature will be examined. It should be noted that the monolayer is optically thin and mostly transparent, so most of this pump-beam passes through it. The monolayer's absorbance would be $\sim 10^{-4}$ so that, in the worst case, only ~ 0.01 mJ/pulse cm^{-2} would be absorbed, leading to a maximum temperature rise of ~ 24 K in the monolayer, taking the monolayer density to be 1 g/cm^3 and the relevant heat capacity to be that of the water subphase. However, since the layer is very thin, the system is not in thermal
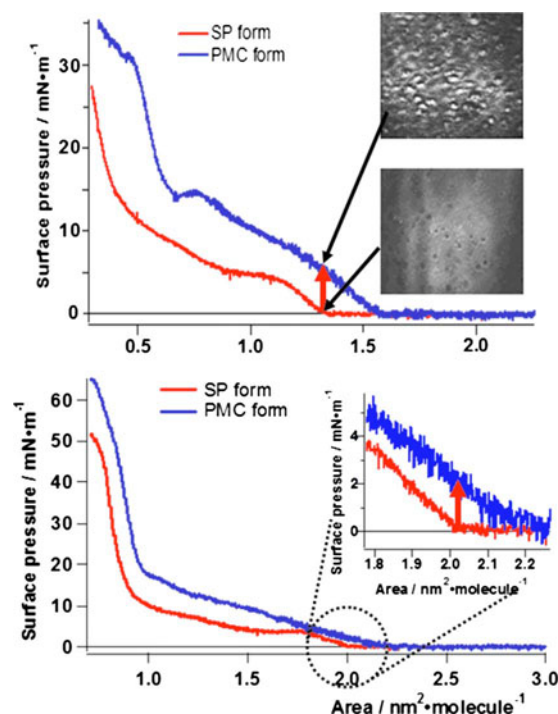

FIG. 1. (Color online) Pressure isotherms: top—pure SP monolayers converting to a mixed monolayer containing PMC; bottom—mixed OD:SP 2:1 converting to the mixed SP PMC-OD layer. Inset images: top—show the results of pulsed laser irradiation of the pure SP monolayer to form the mixed SP PMC layer obtained from time-resolved BAM at 1 μs after irradiation; bottom—shows the monolayer before the pulsed laser has converted from SP to PMC
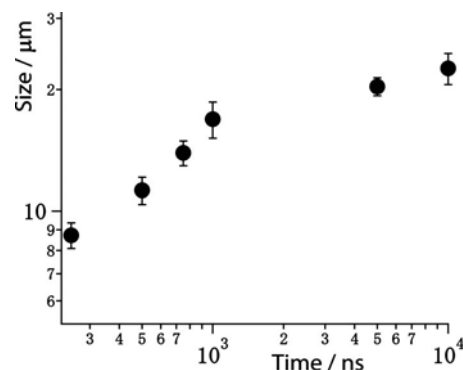

FIG. 3. Log-log plot of domain growth with time for a monolayer of 1:2 OD-SP irradiated at 24 mJ/pulse cm^{-2}.

confinement and the layer will rapidly lose its heat to the subphase almost instantly during the laser pulse. The characteristic thermal relaxation time is given by
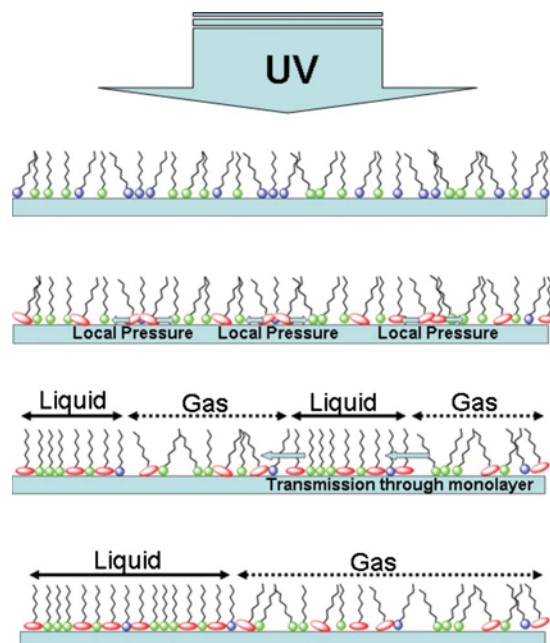
$$t_c = d^2/4\Delta.$$

The thermal diffusivity Δ can be taken to be 1.5 $\times 10^{-3}$ cm^2 s^{-1} (Ref. 27) and d can be taken to be the minimum length in which the laser is absorbed ($\sim$2 nm), in which case the characteristic thermal relaxation time t_c will be 7 ps, which is much shorter than the laser pulse. Hence, we can safely ignore thermal effects and the possibility of schlieren caused by density fluctuations resulting from heating, because all thermal gradients would have equalized within the laser pulse and would not persist for the nanosecond- to microsecond-timescale of our observations.

Next, we will consider demixing. It could be that the wave structure is caused by the formation of chemically distinct domains of the PMC and SP forms of the molecule. It is well known that under certain conditions, this PMC will tend to aggregate upon formation under UV irradiation.[19] However, we should then consider the domain growth rate in the current case. If we assume that the major processes of molecular diffusion, if any, have ended by 100 ns, which is reasonable since the domains are ripening from the time that they are first discernible, then the system can be compared to a three-dimensional demixing liquid. In the case of spinodal demixing in binary liquids, the fastest experimentally achievable domain growth rates were less than a few centimeters per second,[14–16] whereas in the current case, the domain growth rate is 20 m/s. In view of this, it is highly unlikely that the domains currently observed can be made up of chemically distinct compositions of SP and PMC that ripen by being squeezed through interconnected channels as in spinodal demixing. Furthermore, the infinite time situation for the demixing scenario would be the formation of stable aggregates of PMC. However, these aggregates are not seen and the wave structure disappears into the background after $\sim$10 μs.

Therefore, the best explanation for the appearance of the wave structure is that, as expected, we are observing condensation of liquid type domains in a gaslike monolayer, since this phenomenon was only observed where UV light would jump the monolayer from a gaslike to a gas-liquid coexistence-type monolayer. This means that we are observing a phase transition that will be a model for a single component fluid system. This hypothesis will be discussed next.

It is apparent from the images obtained that there are interconnected bright and dark structures that must be created by phases of different densities, giving different reflectivities, lets say gaslike and condensed liquidlike domains. The areas that the gaslike and the condensed domains cover are similar, meaning that neither phase is the minority. The system could be compared to condensation in a real gas or, more generally, to a phase transition in a pure liquid involving density fluctuations. One example of this type of phase transition is in sulfur hexafluoride. For this system, isotropic growth was also determined to occur, as in binary liquids, by the observation of a spinodal ring in the small angle light scattering distribution.[28] The timescale of this type of process is governed by thermal diffusivity and is generally considered to be several orders of magnitude faster than for binary liquid demixing, which is governed by mutual diffusion. However, in the current case, heat dissipation to the subphase will be so rapid that it will probably not be a limiting factor.

During the UV laser pulse, the monolayer in the irradiated area would convert from a stable SP-OD molecular distribution into a stochastic distribution of SP, PMC, and OD. This would result in a change in the molecular interactions in the monolayer since PMC requires more area per molecule, leading to a pressure jump in excess of $\sim$2$\times 10^{-3}$ N m^{-1} based on the equilibrated pressure of the mixed monolayer at this average coverage of $\sim$2 nm^2 per SP. This pressure increase would cause the molecules in the monolayer to form tiny density gradients which would lead to condensed liquidlike phases coexisting with the gaslike phases without the need for molecular or domain diffusion, as shown in Scheme 2. The limiting factor in domain growth in this case is probably the speed of sound in the monolayer as this would be the time it would take for a condensed liquidlike phase to expand to a gaslike phase or a neighboring gaslike domain to be compressed to a liquidlike phase. If domains grow at 20 m/s, then this value would be a good figure for the speed of acoustic pressure waves in the monolayer. This may at first seem to be slow; however, the pressure waves must travel in a thin layer with little inertia on a viscous and high inertia sublayer. Furthermore, Möbius *et al.* already gave a value for the transmission speed of pressure waves in a monolayer of $\sim$5 ms^{-1}.[21]

Since the area fractions of the two phases are similar, this again appears to have similarity to the situation in two- and three-dimensional spinodal demixing or condensation in a

SCHEME 2. (Color online) Proposed mechanism of domain ripening.

single phase system. Indeed, it is apparent that the morphology growth is also isotropic in this case. In spinodal demixing and phase transitions, percolating phases are forced to form since both phases cannot form spherical nuclei because they have similar volume fractions and spheres do not pack well. Similarly, the process of metastable nucleation cannot therefore be occurring in this two-dimensional case and homogeneous nucleation must be occurring. This is because, like spheres, circles will not pack well so the morphology that develops is an interconnected percolating one that is similar to that seen in the later stages of two- and three-dimensional spinodal demixing. In the intermediate and late stages of three-dimensional spinodal demixing, molecular diffusion is less dominant and hydrodynamic effects, which are governed by the need to reduce surface pressure, control the domain growth.[29–31] In these later stages, material is squeezed from high curvature regions to lower curvature regions, but the liquid material must move in channels and against another liquid so that viscous forces dominate, since the phases have different compositions.[14–16] If the domains move fast enough, then inertial effects may come into play.[30,31] However, this has never been seen in practice.[14–16]

In principle, these later stages of three-dimensional demixing may have similarities to all expected stages of the mechanism in the monolayer since the molecules in the monolayer never really needed to diffuse on the molecular level as they are instantly (within the UV laser pulse) created with a statistically uniform composition throughout the monolayer. However, this new composition, once formed, was unstable and formed liquidlike domains in the gaslike surroundings. In order for such domains to ripen in the monolayer, it would not be necessary for the material in the different domains to move over great distances to merge with other similar phases. Instead, small domains can potentially push against neighboring domains squeezing domains further away, at some distance, even without the individual molecules themselves diffusing into a different spatial region of the irradiated area. In other words, the process that is proposed is cooperative and could occur mediated through pressure at a distance and be limited by the speed of travel of pressure waves. The current proposed system is therefore somewhat different from binary mixtures and three-dimensional condensation in the early stages and even in the later stages, where viscous forces dominate under most experimentally achievable conditions. However, some similarities may still exist in terms of the evolving morphology and the growth rate.

In the case of demixing binary mixtures, the expected growth would be expected to have an exponent of 0.5 in the later stages in two-dimensional demixing (before inertial effects).[1,4,5] In the current case, the initial exponent is close to 0.5. Further, in the later stages, the growth rate slows, as predicted for inertial growth;[30,31] however, no evidence of turbulence is seen in our images, which is the usual explanation for late stage slowing. Hence, we should estimate the Reynolds number in a monolayer at an air/water interface as follows:

$$R_e = F_{\text{inertia}}/F_{\text{viscous}}.$$

F_{inertia} can be estimated as $F_{\text{inertia}} \sim \rho_2 L V^2$, where ρ_2 is the two-dimensional density of a monolayer, L is the size of a monolayer domain, and V is the velocity of the domain.

For F_{viscous} in our system, there are two viscous forces which are applied to the monolayer's domains. These are the viscous force from the water substrate (F_{viscous1}) and the viscous force from the domain environment inside the monolayer (F_{viscous2}): $F_{\text{viscous-total}} = F_{\text{viscous1}} + F_{\text{viscous2}}$.

$F_{\text{viscous1}} \sim \eta_w L V$, where η_w is the viscosity of water ($\sim 10^{-3}$ kg m^{-1} s^{-1}). L, the domain's size, has an order of magnitude ~ 20 μm in our experiments in later times. V is the velocity of domain growth (~ 20 m/s).

$F_{\text{viscous2}} \sim \eta_s V$, where η_s is the shear "two-dimensional" viscosity. Then $F_{\text{viscous2}}/F_{\text{viscous1}} = \eta_s/\eta_w L$. $\eta_s < 10^{-9}$ N s m^{-1},[32] $\eta_w = 10^{-3}$ N s m^{-2},[33] and $L \sim 10^{-5}$ m. This means that $F_{\text{viscous2}}/F_{\text{viscous1}} < 0.1$. Therefore, we can neglect F_{viscous2}. This means that if $R_e = \rho_2 L V^2/\eta_w L V = \rho_2 V/\eta_w$ with $\rho_2 \sim 10^{-6}$ kg/m^2, R_e is only $\sim 10^{-2}$ even at velocities of ~ 20 m/s. In this case, turbulent effects would certainly be absent, as observed experimentally.

It is noteworthy that the wave structure remained broadly confined within the irradiated area even over 10 μs. However, we must expect that by jumping between isotherms, we would create a pressure exerted outward from the irradiated region. The eventual equilibrium state must therefore result from the irradiated region, returning to a gaslike state by traveling back down the isotherm of the PMC-SP mixture until the pressure between the irradiated region and the surroundings becomes equalized by expansion. However, that expansion rate can only be expected to be similar to the rate of domain growth within the irradiated area, which is actually the rate of acoustic relaxation governed by the speed of sound. In the current work, the domain size is of the order of 20 μm after 10 μs. At this expansion rate, for the entire irradiated region, we would not have expanded much compared to the irradiated area of 400 μm. In fact, it would only grow by about 7% over 10 μs. The characteristic acoustic relaxation time will be given by $t_{\text{ac}} = d/c$, where d is the shortest dimension or the radius of the spot, since the wave propagates laterally and not into the subphase, and c is the speed of sound, which we can take to be ~ 20 ms^{-1}. Hence, the acoustic relaxation time would be ~ 10 μs, which is quite consistent with the observation that after 10 μs the wave structure has all but vanished. We can therefore suggest that the slowing of the domain growth after 1 μs is in fact caused by loss of pressure from the irradiated regions to the surroundings, occurring at a similar rate to the domain growth rate, rather than inertial effects.[30,31]

IV. CONCLUSION

In conclusion, we have observed cooperative isotropic phase domain growth in a two-dimensional system. The rate of domain growth is much faster than observed in superficially similar systems, such as demixing binary mixtures, leading us to suggest that the domains grow due to longitu-

dinal pressure transmission in the monolayer. In this case, the rate of domain growth should indicate the expected rate of signal transmission in a monolayer, which is effectively the speed of sound in the monolayer (~ 20 ms^{-1}). This would have important implications for signal transmission in biological membranes.

ACKNOWLEDGMENTS

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