

LETTERS

Measurement of Line Tension from Cell Coalescence Events in a Langmuir Film

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Received: October 27, 1995; In Final Form: April 30, 1996[®]

Epifluorescence microscopy was used to examine Langmuir films of an alkoxy-substituted (phenylene acetylene—pyridine acetylene) polymer. The polymer was observed to form microscopic two-dimensional emulsion-like cellular network morphologies after treatment by a simple processing procedure. Cell coalescence was found to be an important process in the evolution of the cellular network. As observed under the microscope, cell coalescence is similar to the bursting of a soap bubble. An estimate of the line tension was made using an analogue of an equation developed by Culick and others to describe the rim velocity of a bursting soap bubble.

Introduction

In the present work, epifluorescence microscopy was used to examine Langmuir films of an alkoxy-substituted (phenylene acetylene—pyridine acetylene) polymer (Figure 1). The polymer was observed to form microscopic two-dimensional emulsion-like network morphologies after treatment by a simple processing procedure. Other related properties of the polymer's network, including the network dynamics, will be reported elsewhere.¹ Cell coalescence was found to be an important process in the evolution of the cellular network.

Cell coalescence is believed to begin at corrugations in edge width. If the increase in Gibbs line energy and dipole—dipole interaction energy is exceeded by a decrease in the van der

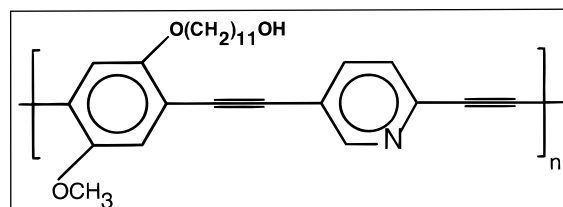


Figure 1. Cellular network-forming polymer used in this study.

Waals energy, then the corrugations will grow in amplitude resulting in breakage of the cell edge and coalescence. Once the edge is broken, the Gibbs line energy and the van der Waals energy (to a much lesser extent) drives the material from the broken edge into the vertex.²

[®] Abstract published in *Advance ACS Abstracts*, August 15, 1996.

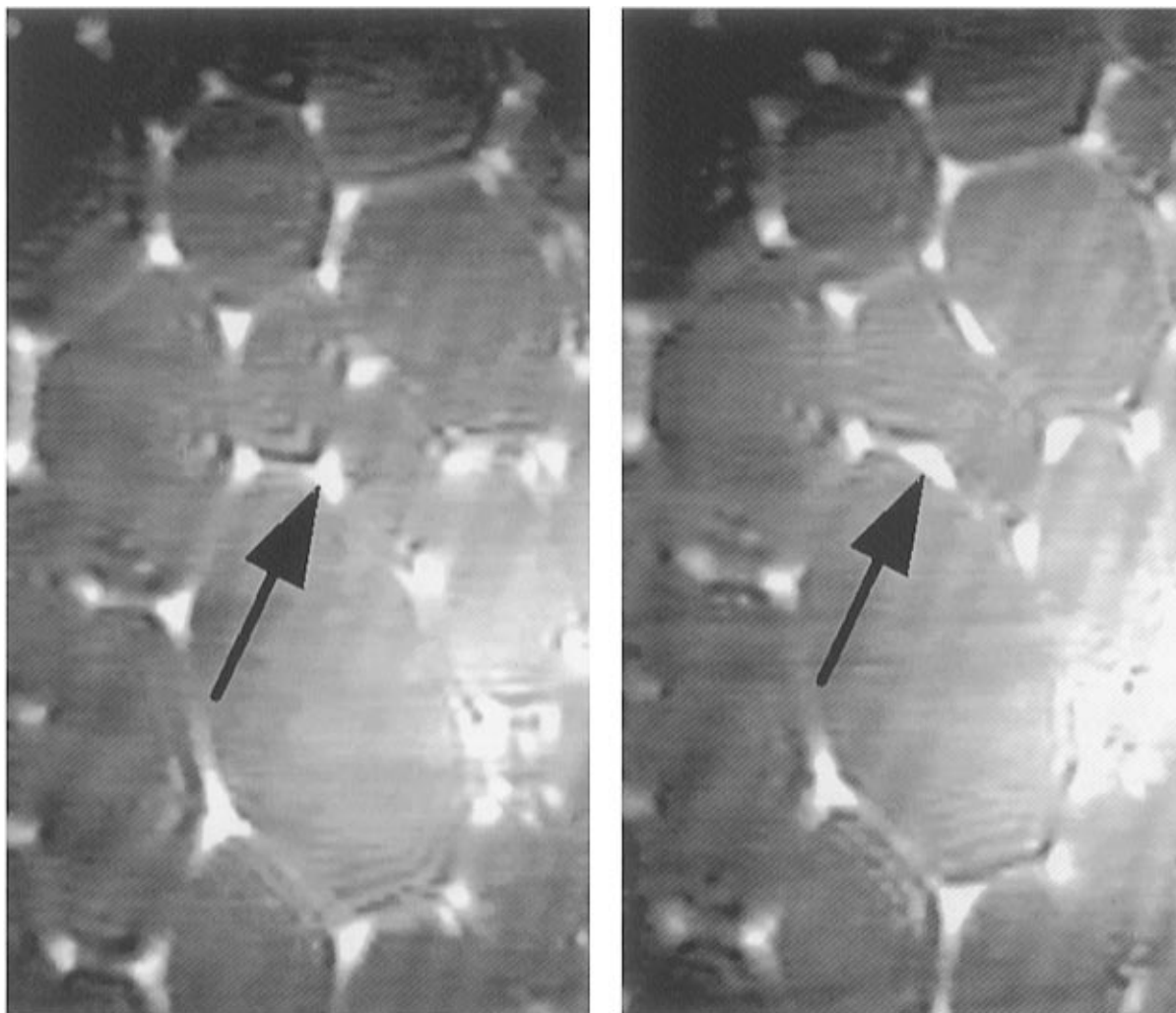


Figure 2. Epifluorescence micrographs of a cell coalescence event (at arrow): (a, left) before; (b, right) after.

Experimental Section

An 8×17 cm PTFE trough (KSV Instruments) with a quartz window in the bottom and enclosed in a plexiglass box was attached to the stage of a Nikon DIAPHOT-TMD-EF inverted epifluorescence microscope. A single PTFE barrier was used to compress the film. The microscope was fitted with the B-2A filter block which provides excitation wavelengths between 450 and 490 nm and allows observation of emission wavelengths greater than 500 nm. The dynamics of the cellular network were recorded on videotape using an Optronics VI-470 remote-head microscope camera (Optronics Engineering) and subsequently transferred to a Sun Sparcstation 1 using a VideoPix image capture board for image analysis (PV-Wave).

Discussion

As observed under the microscope, the polymer's cellular network consists of two isotropic fluid phases: a more expanded (ME) phase and a more condensed (MC) phase. Cell coalescence in the polymer's cellular network is similar to the bursting of soap bubbles. When the edge between two neighboring cells breaks, it rapidly retracts toward the former vertex. The rapidity of the process, captured in real time through a series of video frames (Figure 2), is testament to the magnitude of the line tension existing between the two phases. An estimate of the line tension may be made using an analogue of an equation first developed by Culick to describe the rim velocity of a bursting soap bubble.³

TABLE 1: Comparison of Calculated Line Tension between Monolayer Domains

material	monolayer phases	line tension (mN)	ref
nitrobenzene-oxadiazole stearic acid	solid/liquid	10	5
cholesterol/dimyristoylphosphatidylcholine 3:7 mixture	liquid/liquid	10^{-7} – 10^{-8}	11
cholesterol/dimyristoylphosphatidylcholine 3:7 mixture	liquid/liquid	10^{-10}	7
poly(dimethylsiloxane)	liquid/gas	10^{-10}	8
poly(hydroxyundecanoxylphenyleneacetylenepyrindineacetylene)	liquid/liquid	10^{-10}	1

Figure 3 depicts a small section of the ruptured cell edge. The ruptured cell edge moves along the axis s . An incremental slice of the edge is denoted as ds . The initial width and length define w and s .

The momentum balance, assuming the velocity, $U = \text{constant} = ds/dt$ and including the viscous drag force gives where U is the velocity of the edge, γ is the line tension, Γ is the surface concentration (see supporting information):

$$\gamma = \frac{1}{2}(\Gamma w U^2 + F_D)$$

There are at least two types of viscosity opposing the retracting edge. These are the surface shear viscosity of the polymer layer, ν_s , and the shear viscosity of the water subphase which may move with the polymer layer, ν_b . Typical values found for these viscosities are $\nu_b = 10^{-2} \text{ g cm}^{-1} \text{ s}^{-1}$ and $\nu_s = 10^{-2} \text{ mg s}^{-1}$.⁴ Slippage of the polymer layer over the water

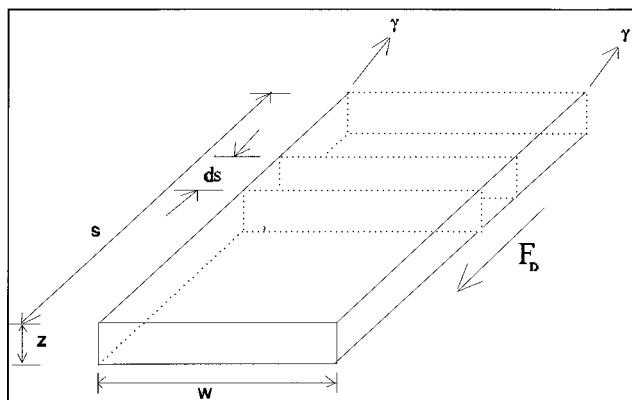


Figure 3. Idealized section of ruptured cell edge.

subphase as well as slippage of the MC phase past the ME phase are assumed to be negligible.

The viscous drag force due to ν_b may be estimated by assuming the retracting edge is a finite flat plate, for which, the Reynolds number is

$$Re = U\rho s/\nu_b$$

where ρ and ν_b are the density and viscosity of water, respectively. The equation for the drag on one side of a finite flat plate oriented parallel to the direction of flow with a Reynolds number less than 500 000 is

$$F_D = (1.328/2)wsU^2\rho Re^{-0.5}$$

Observing U to be 1000 $\mu\text{m/s}$ for an edge 7 μm wide and 100 μm long, the Reynolds number was calculated to be 0.1. With the density and viscosity of water at 1 g/cm^3 and 0.01 g/(cm s) the calculated viscous drag force was 1.4×10^{-12} N. The surface concentration of the MC phase was found to be 2.1 repeat units/ nm^2 , so this leads to an estimated value of 7×10^{-10} mN for the line tension. For purposes of comparison, several values of the line tension estimated by other workers using other techniques is shown in Table 1.⁵⁻⁸

The magnitude of the line tension has an important effect on the cellular network dynamics and topology. High values of line tension favor small domain sizes. The value estimated here is intermediate between the low values found for poly-(dimethylsiloxane) and the high values found between the solid and liquid phases of stearic acid. High values of line tension lead to more circular domains. In this polymer, the convolution index was close to the value for circles (1.0) but not as close as that found for lipid monolayers.⁹ In general, a measured line tension may depend on domain size and shape.¹⁰ The line tension has been estimated only for one point in the phase

coexistence region of PPEHU. Thus it is difficult to speculate about any links between the magnitude found and the composition of the two phases or the effect on hysteresis in the measured surface pressure observed in compression/expansion cycles.

This method for estimating the line tension between 2D phases in Langmuir monolayers is unique, although it draws strongly from similar models developed for 3D ruptured soap bubbles. The method of other workers in which domains are intentionally distorted from the usual circular shape by an air stream into long thin bola shapes is mathematically similar, particularly in its difficulties with unknown values for the various viscosity coefficients.¹¹ Estimating line tension based on observed cell coalescence events requires greater patience than other methods because the event must happen within the field of view of the microscope. Also the event must be recorded so that frame-by-frame measurement of the retracting cell edge may be made. Its main advantage over some of the other techniques is that the monolayer need not be disturbed from its normal state. The accuracy of the technique could be improved by utilizing faster video recorders to capture more frames per event and also if better estimates of the viscosity were available.

Acknowledgment. This work was supported by a grant from NASA (Grant NASA NCC3-255). The polymer sample was synthesized by Dr. J. Le Moigne and Dr. M. Moroni at the CNRS Materials Research Institute in Strasbourg, France through funding from the NSF US/France program (Grant INT9216979). The authors wish to thank Dr. Tom Stephens for a critical reading of the manuscript. The authors acknowledge Dr. Stefan Setz for capturing the video stills used in Figure 2. Visual Numerics and Micron Technology Inc. are acknowledged for technical assistance.

Supporting Information Available: Detailed derivation of the momentum balance equation (4 pages). Ordering information is given on any current masthead page.

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