# Evolutive Dissipative Structures in Photopolymerized Polyacrylate Films

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Evolutive dissipative structures were observed during UV irradiation of the surface of acrylate films leading to photopolymerization. Self-organization results in the formation of hexagonal or square cells, waves, stars, and spots. These different situations were observed on the same polymer mixture. Thermodynamics of relief formation was applied to these peculiar cases. Evidence was provided for the influence of surface adsorption and bulk viscosity.

## I. Introduction

Self-organization of liquid surfaces and interfaces under the influence of various horizontal or vertical gradients due to matter or heat transfer has been observed during evaporation of a liquid layer, in drying of painting films, or in biologic tissues for example, and the thermodynamics of the irreversible process is well-adapted to such phenomena. The presence of various types of structures such as hexagonal cells, waves, or even spots is well-known. A thermodynamics of hydrodynamic instabilities has been proposed by Glansdorff and Prigogine[1] and Nicolis and Prigogine[2] examined the case of spatial structuring through chemical reactions essentially.

The thermodynamics of self-organization at the surface of UV photopolymerized polyacrylate films has been reported on recently[3,4] in connection with the existence of various surface structures. The thermodynamics of irreversible processes is well-adapted to the analysis of such surface phenomena occurring on ca. 50 $\mu$m thick films.[5] When the surfaces are in contact with various atmospheres, a complementary behavior is observed due to the influence of adsorption and diffusion at the air−polymer interface.[6]

Such situations appear under various constraints and are commonly observed under evaporation of organic solvent mixtures deposited as layers,[7] and the layer thickness is then a major parameter. So polyacrylate mixture films exhibit self-developing properties due to hydrodynamics and surface free energy effects of Marangoni type,[2,6] leading to a periodical relief. The profile generated by alternated irradiation through a lined mask varies from a perfectly sinusoidal shape to a complex sinusoidal one or even a crenel as reported elsewhere by the authors.[5,6]

A thermodynamic theoretical analysis of the wave formation and turbulence at the interfaces has been proposed by Velarde and Chu.[8] Thermal or solutal gradients give rise to convective patterns, waves, and sometimes turbulence. A theoratical analysis based on the treatment of liquid interfaces as genuine oscillators was developed, and the role of surfactants present at the interface was taken into account.

The aim of the present work is to substantiate the existence of these various situations for the same polyacrylate mixture by varying the experimental conditions of UV irradiation, the composition, and the film thickness. An acrylate mixture containing eosine as a photosensitizer has been developed and

**TABLE 1**

|  | formulation I | formulation II |
|---|---|---|
| oligourethane diacrylate (Mw, 1200; viscosity, 2100 mPa·s at 60 °C) | 36 | 48 |
| tripropylene glycol diacrylate | 36 | 24 |
| 2-(2-ethoxyethoxy)ethylacrylate | 23.5 | 23.5 |
| dimethylamino ethylacrylate | 1 | 1 |
| 1-phenyl-2-hydroxy-2-methylpropanone | 3.5 | 3.5 |

subjected to UV irradiation on its whole surface, contrary to previous experiments performed with UV irradiation through a lined mask. The sample can thus be investigated either in the case of hydrodynamic instabilities, which can lead to turbulence, or under conditions of stability.

With acrylate films, there is a modification of the viscosity of the mixture during the photopolymerization because of the cross-linking. The apparition of organized structures as a function of time in the fluid film is examined as a function of time, and after hardening of the mixture, these stuctures become permanent. The different situations prevailing after photochemical treatment show the gradual change from cellular patterns to a plane surface, without any deformation, by gradually varying the preparation conditions.

## II. Experimental Part

**II.1. Material.** An acrylate−eosin mixture was prepared with stirring at 25 °C. The photocurable formulation contained a mixture of multifunctional acrylates and an initiating system. Two formulations referred to as I and II were used; the composition (weight per weight percentages) is given in Table 1. The concentration of the sensitizer (eosin Y) corresponded to an optical density of 0.2 at 514 nm for a film of thickness 30 $\mu$m.

The formulation (80 or 150 $\mu$m) was coated onto glass slides with the doctor−knife technique and left for a while under inactinic conditions so as to obtain a constant thickness of the resin film.

**II.2. UV Irradiation.** The samples were cured on a belt conveyer under a high-pressure mercury arc (IST UV Lamp type M200 U1) whose lines are centered at 313, 328, and 365 nm. The illuminator is an IST Strahlentechnik GMBH one. The light source is at the focus of a parabolic reflector and ensures a quasi-homogeneous fluence of 200 mW·cm$^{-2}$ at the

Photopolymerized Polyacrylate Films

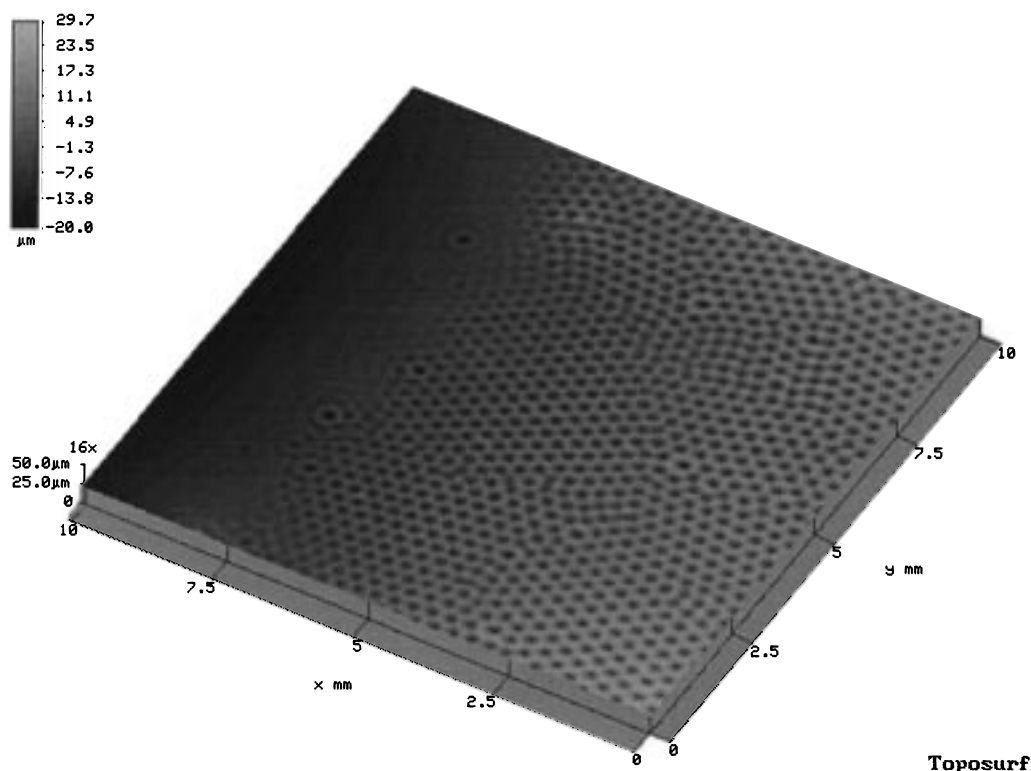*J. Phys. Chem. B, Vol. 102, No. 40, 1998* **7715**



**Figure 1.** Surface without deformation on a part of the sample obtained with formulation I in 3D representation.

**TABLE 2: Different Types of Relief on the Acrylate Samples**

| sample[a] | thickness ($\mu$m) | speed (m·min$^{-1}$) | incident density of dose exposure (mJ·cm$^{-2}$) | relief shape |
|---|---|---|---|---|
| A (II) | 140 | 30 | 58 | cells |
| B (I) | 130 | 25 | 65 | cells |
| C (I) | 150 | 40 | 50 | chevrons |
| D (I) | 80 | 50 | 42 | chevrons, stars, and cells |
| E (I) | 87 | 40 | 50 | chevrons |

[a] Two formulations: I and II.

sample surface. The distance light source sample is maintained at 15 cm. The belt speeds available were from 25 to 50 mm·min$^{-1}$, and under the photonic conditions of the experiment as given before, the incident dose of actinic light received by the samples when passing through the light oven ranged from 35 to 65 mJ·cm$^{-2}$ as a function of conveyer speed. Correlation between speed and density of the dose exposure for a given geometry is given in Table 2.

**II.3. Surface Relief Analysis.** The relief resulting from the combined effect of photochemically induced reactions and hydrodynamics at the polymer surface was analyzed with an optical profilometer from UBM Messtechnik GMBH. A red laser beam at 780 nm was reflected at the surface of the photopolymer, and the difference in height was determined by automatic shifting of a lens to always keep the surface at the lens focal distance.

Different kinds of images were obtained by analyzing the surface with a red laser beam. A 2D height profile was obtained, and 3D pictures were recorded at the 100 $\mu$m scale.

**III. Results**

Different shapes of relief were observed on irradiation: uniform surfaces with no deformation, concentric cercles,

hexagonal cells, star-shaped waves, parallel waves, orderly arranged waves sometimes called shark skin, and even spots. All these results are shown successively and sometimes on the same samples in Figures 1−5. Overstructures with symmetry of order 3 can appear as shown on Figure 1, and isolated spots can be present.

For a sample irradiated at a 60 mJ·cm$^{-2}$ energy with a translation speed of 25−30 m·mn$^{-1}$ on a 4 cm long path, Bénard type hexagonal cells[9,10] hollow in their center were observed.

Surfaces were examined as a function of film thickness (80−150 $\mu$m), irradiation intensity (40−65 mJ·m$^{-2}$), and translation speed (25−50 m·mn$^{-1}$) as precised in Table 2.

The thickness of the deposited film is an important parameter for relief development: as the thickness increases, the relief becomes more disorderly, as shown in Figure 6, when going from cells to waves. When working under static conditions of irradiation, the same type of relief appears at the film surface for an identical irradiation time.

A good reproducibility of the sample surface organization has been achieved by the lone control of the conveyer speed or of the irradiation time in static conditions.

**IV. Thermodynamics of Surface Behavior[8]**

Convective instabilities were observed on liquid layers with a surface open to air and affected by thermal or surfactant gradients. Steady convective patterns appear, as well as oscillations, waves, and even turbulence. Relationships governing such situations have been reported.[8] The surface deformation depends on the stress at the liquid surface. Transverse motions such as ripples[11] and also longitudinal motions[12] have been observed, the latter corresponding to Marangoni and Lucassen type waves. According to the observations, the frequency of the longitudinal waves depends on viscosity and elastic modulus of the surface, whereas transversal waves depend
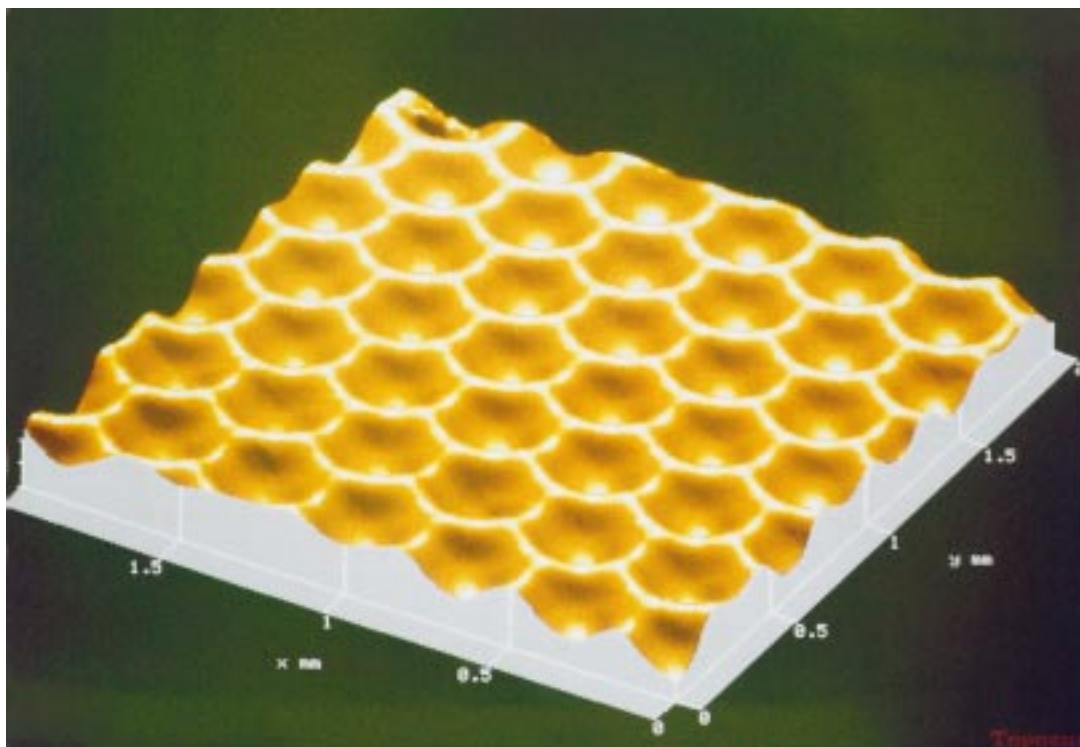
**Figure 2.** Hexagonal cells with 40 $\mu$m high configuration obtained with formulation II in 3D representation.
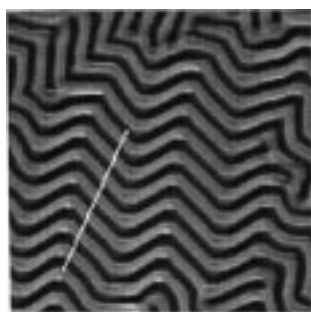


**Figure 3.** Parallel waves configuration obtained with formulation I on a $5 \times 5$ mm$^2$ area in 2D representation.

on gravity and surface free energy. These waves can be sustained if large gradients are present in the liquid in a given direction.

Velarde and Chu[8] have suggested that liquid interfaces could be treated as oscillators. The authors use this linear approach, hereafter considering that the acrylate layer can be treated as a layer with polar species at the surface modifying the superficial free energy as a surfactant would do. The less viscous outer layer is the result of the presence of oxygen in the surrounding atmosphere, having an inhibiting effect on the cross-linking, and there is concentration of oxidized species at the surface.

**Equations of Surface Behavior.[8]** A liquid layer open to air excited with thermal or surfactant gradients can present convective instabilities, and liquid interfaces are treated as genuine oscillators. The presence of a surfactant monolayer induces elastic properties of the surface. Consider first a liquid layer with infinite depth. As an example, a simple linear oscillatory system can be described by a harmonic equation:

$$\frac{\partial^2 f}{\partial t^2} + \phi f = -\Psi \frac{\partial f}{\partial t} \qquad (1)$$

while $f$ is the unknown, $\Phi$ and $\Psi$ are factors specific to each case.

When $\Psi$ is positive, the motionless state is asymptotically stable, and when $\Psi$ is negative, oscillatory explosion takes place. For $\Psi = 0$, there is a sustained oscillation.

If one takes the surfactant concentration, $c$, at the surface as the relevant variable in the harmonic oscillator, the following equation is obtained:

$$\frac{1}{[2S\omega]^{1/2}}\left(SHz\,\frac{\partial^2 c}{\partial t^2} + \frac{Ea^3}{S\omega}c\right) = -\left(1 + \frac{Ea^2}{S^{3/2}\omega^2}\right)\frac{\partial c}{\partial t} \qquad (2)$$

where $S = \nu/D$ is the Schmidt number, with $\nu$ being the kinematic viscosity and $D$ the mass diffusivity; $Hz = k^l/l$ is the Langmuir adsorption number, with $l = [T_0/\rho g]^{1/2}$ being the capillary length, $T_0$ being the surface free energy, $k^l$ being the Langmuir adsorption constant, and $a$ being the Fourier wavenumber; $E = -(dT/d\Gamma)_0 k^l \beta^c l^2/\eta D$ is the elasticity (surfactant Marangoni) number, with $T$ being the surface free energy, $\Gamma$ being the adsorption, and $\beta^c$ being the gradient of surfactant at the quiescent state; $\eta = \rho\nu$ the dynamic viscosity, $\rho$ being the density; and $\omega = Im\,(\lambda)$ is the imaginary part of $\lambda$, where $\lambda$ is the time constant of the solution of the equations, that disturbances comply with at the quiescent state.

For *longitudinal waves*, if in order to simplify the problem it is supposed that the deformability of the surface has negligible influence on the longitudinal wave motion, when energy dissipation and Marangoni work compensate each other, according to the developments in a linear approximation,[8]

$$1 + \frac{Ea^2}{S^{3/2}\omega^2} = 0 \qquad (3)$$

when $-E > S^{3/2}\omega^2/a^2$, an explosion or turbulence ensues; when $-E < S^{3/2}\omega^2/a^2$, the motion is damped; and in the neutral case of stability,

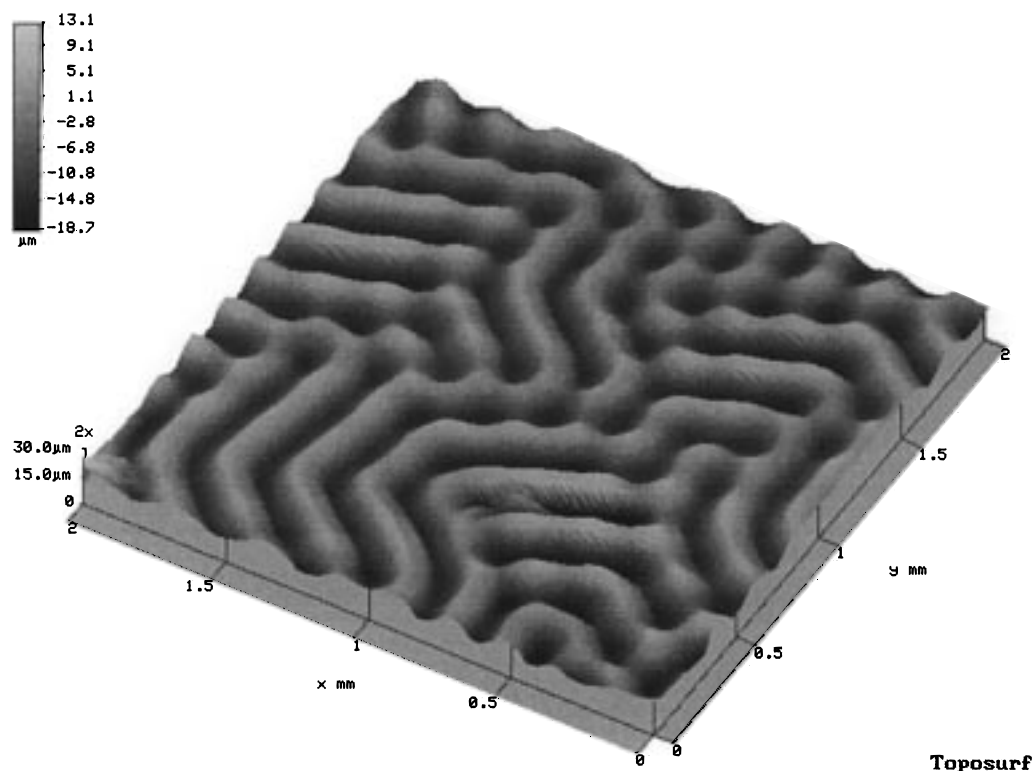$$SH_z\omega^2 + \frac{Ea^3}{S\omega} = 0 \qquad (4)$$

Photopolymerized Polyacrylate Films

*J. Phys. Chem. B, Vol. 102, No. 40, 1998* **7717**



**Figure 4.** Stars and waves configuration obtained with formulation I in 3D representation.
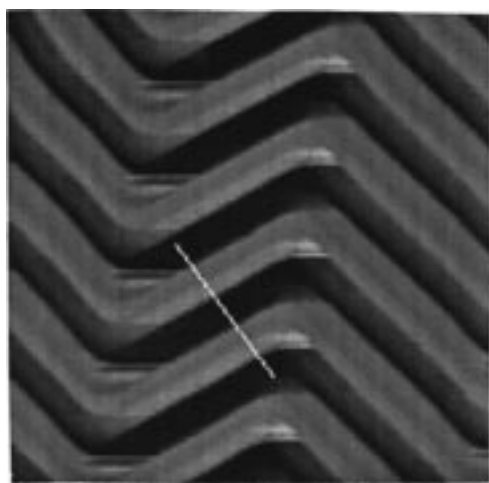


**Figure 5.** Regular disposition of waves obtained with formulation I on a $2 \times 2$ mm$^2$ area in 2D representation.

Equations 3 and 4 describe the oscillating state at the air−liquid interface. When $\omega = 0$, a transition from a steady state of rest to a steady cellular convective pattern can be predicted.

Taking into account expression 3, one can write

$$(\partial T/\partial \Gamma)_0 k^1 \beta^c l^2 / \eta D \underset{<}{\overset{>}{\phantom{=}}} \frac{S^{3/2} \omega^2}{a^2} \qquad (5)$$

Thus depending on the value of the elasticity number, different types of organization can prevail at the surface. If motion is damped, no relief appears, and in the neutral case of stability, the equation is modified and a relief corresponding to a sustained oscillation is maintained.

The number $E$ is a function of adsorption and an inverse function of viscosity and diffusivity. If the $(dT/d\Gamma)$ term is negative due to adsorption, the system is fairly damped and no relief takes place.

If the term is positive, turbulence can appear. When the two terms in eq 5 are equal, a neutral state of stability corresponds to a sustained oscillation at the free surface as given by Velarde and Chu[8] in a linear approach.

A first approach is thus given through the adsorption properties. Another takes into account the effects of viscosity and diffusivity.

Equation 5 can be written in the form

$$(\partial T/\partial \Gamma)_0 k^1 \beta^c l^2 \underset{<}{\overset{>}{\phantom{=}}} \frac{(\nu/D)^{3/2} \rho \nu D \omega^2}{a^2} \qquad (6)$$

For the same adsorption term, if the viscosity is high, the system is fairly damped and exhibits an even surface. If the viscosity is low, it tends to be turbulent with possible appearance of spots as isolated protuberances corresponding to the stage before turbulence. Two main variables are found: the adsorption in the left hand side member and the bulk viscosity and the connected diffusion in the right hand side member. Predictions can be made as follows:

(a) If adsorption lowers the surface free energy, for the same viscosity the system is damped without relief and in the opposite case, turbulence appears, and in a first stage waves or spots could be present, these spots corresponding to volcanos geometry.

(b) If bulk viscosity is higher, for the same adsorption, the diffusion can be lowered and the quotient $\nu/D$ decreases, so that the system becomes turbulent, and if bulk viscosity is lower, the diffusion coefficient decreases and the system is fairly damped.

All this can be verified by UV irradiation experiments, because the adsorption term is governed by the photochemical reaction at the surface.

Transverse waves can also be observed according to ref 8. The oscillatory convective motion of the surface can be written as:
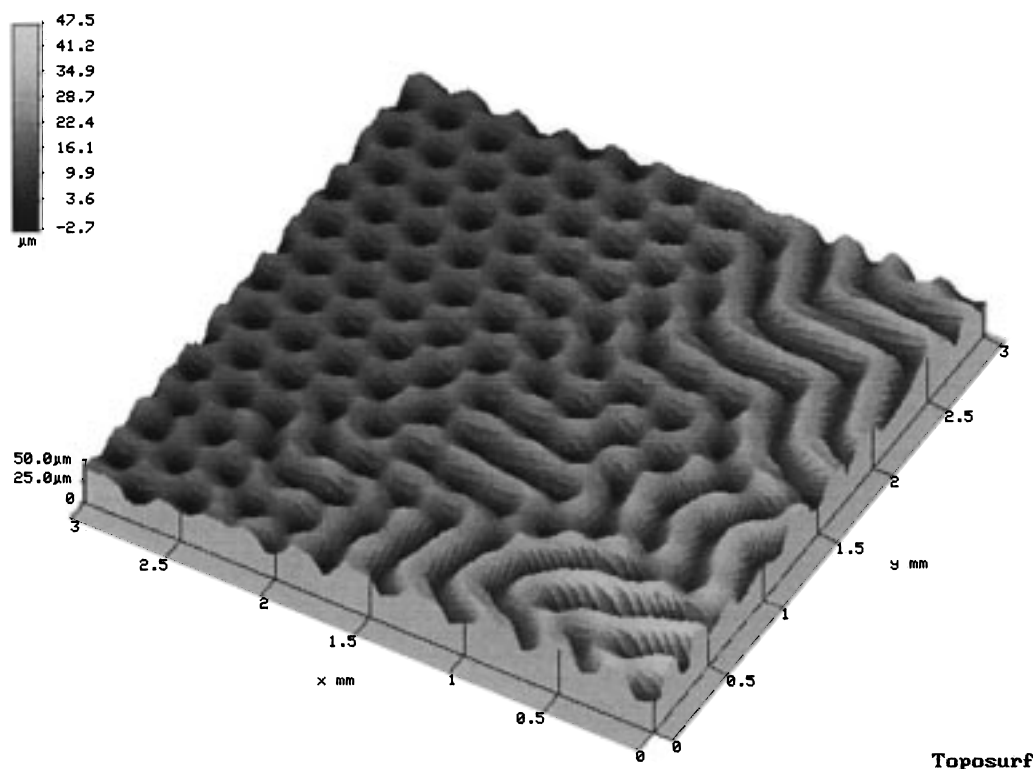
**Figure 6.** Relief evolution as a function of film thickness obtained with formulation II in 3D representation.

$$\frac{d^2\zeta}{dt^2} + \frac{\beta_0 + a^2}{SC}a\zeta = -\left(4a^2 + \frac{Ea^3}{S\omega[2S\omega]^{1/2}}\right)\frac{d\zeta}{dt} \quad (7)$$

where $\beta_0 = \rho g l^2/T_0$ is the bond number $C = \eta D/lT_0$ is the capillary number.

When

$$-E < 4S\omega[2S\omega]^{1/2}/a \quad (8)$$

the oscillation will be damped, and when

$$-E > 4S\omega[2S\omega]^{1/2}/a \quad (9)$$

the oscillation grows exponentially.

The neutral state corresponds to the critical threshold of instability and then

$$-E = 4S\omega[2S\omega]^{1/2}/a \quad (10)$$

The critical value for sustained transverse waves, i.e., oscillations, is

$$E_c^T \cong -7.931(S/C)^{3/4}$$

$$\cong -7.931\frac{v/D}{\eta D/lT_0} = -7.931\frac{lT_0}{D^2}$$
$$(11)$$

The conclusions are similar to those for the longitudinal waves regarding the influence of adsorption and viscosity on the stability of the system.

It is therefore possible to predict the formation or the absence of relief figures, by only taking into account the influence of surface adsorption and bulk viscosity.

Hexagonal cells, stars, and 6-fold stars correspond to the existence of both transversal and longitudinal waves, and parallel waves correspond to the absence of one of either type.

It is well-known that the layer thickness plays a role in the formation of the relief: for a thin layer and a given value of the thickness, no relief appears[13] and the deformation is concave when it develops, whereas it is convex for a thick layer, the deformation depending then on the respective actions of surface tension and buoyancy forces.[15] This is another theoretical approach of the surface evolution, taking into account only surface properties and bulk viscosity in the mechanical hydrodynamic sense.

Relief thus develops for a sufficiently thick layer, and the oscillation grows when adsorption increases the surface free energy and/or when the bulk viscosity is lower. These two entities depend on the composition of the photopolymer mixture and the irradiation conditions, which at first should modify the surface properties. Experimental results will now be examined in the light of these theoretical previsions.

Whatever the model taken into account, one of the parameters which control the surface behavior is always a typical surface property and the bulk viscosity is chosen as the second one. The Hennenberg et al.[8] model, which has been used[5] only, takes into account surface properties and the density of the two superposed layers. This is another way to modelize the film deformation, and in addition, the existence of one type of waves only was assumed in our analysis.[5]

In the present study, owing to the difference of properties in the bulk of the two types of film that were investigated, a more general model was chosen where the Marangoni elasticity number $E$ appears. This allowed an additional approach of the acrylate system under consideration.

## V. Discussion

Taking into account the influence of adsorption and bulk viscosity on the behavior of the acrylate layer alone makes it possible to predict the potential for deformation which can be expected.
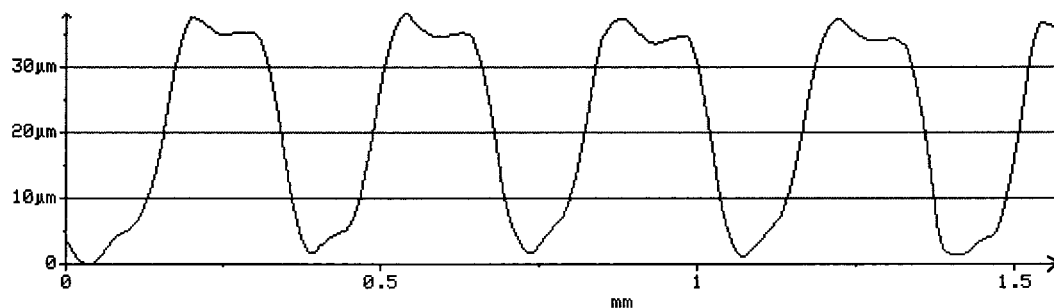
Photopolymerized Polyacrylate Films

*J. Phys. Chem. B, Vol. 102, No. 40, 1998* **7719**



**Figure 7.** Crenel type profile for chevrons.

Simplifying the problem raise by the main variables in the Marangoni term $E$, such as surface free energy $T$, adsorption $\Gamma$, kinematic viscosity $\nu$, and diffusion coefficient $D$, different situations can appear in accordance with eqs 3 and 4.

If the viscosity increases, the diffusion coefficient is lower and $\nu/D$ increases. Then, depending on the variation $(dT/d\Gamma)$, the system becomes damped if there is a decrease, whereas it remains fairly stable if there is an increase.

If the viscosity decreases, the diffusion coefficient is higher and $\nu/D$ decreases. Then the system remains fairly stable if $(dT/d\Gamma)$ decreases, whereas turbulence can appear if it increases.

It is reasonable to assume that the photopolymerization leads to increased surface free energy through cross-linking and the presence of oxidized species at the polymer surface. Thus a higher bulk viscosity of the sample leads to a fairly stable system under UV irradiation and a lower viscosity favors turbulence and less regular surface deformations.

This was shown above with acrylate layers under different conditions of preparation and irradiation. If the viscosity alone is modified, it is possible to state the different behaviors as shown in Figures 1−5.

Following irradiation, a plane surface corresponds to a stable system. The next step is the appearance of concentric circles, hexagonal cells, and parallel waves, and increasing instability goes in hand with the formation of stars and more rarely spots with a volcano type form.

Trends only can be outlined, the exact values of surface free energy, adsorption, viscosity, and diffusion being unknown.

When longitudinal waves alone are present, these parameters control relief formation. Transverse waves are damped for high-viscosity films with decreasing surface free energies, due to adsorption. The oscillation for the same reason in the opposite case grows for low-viscosity and increased surface free energy through adsorption. This can be verified by changing the viscosity of the polymer layer by diluting the acrylate with a solvent. Two formulations were used with different viscosities, and evolution rules relative to the enumerated parameters were similar for longitudinal and transverse waves.

The obtained results are shown in Table 2 for the two formulations I and II, tested at different thicknesses and speeds of linear displacement which condition the delivered intensities.

Formulation I is less viscous than formulation II: 120 and 290 cP, respectively, at 20 and 5 °C.

With formulation I, cells, stars, and chevrons were observed, depending on experimental conditions. With formulation II, cells only were observed under the stated conditions. The speed of the linear movement of the sample subjected to irradiation had a direct influence on the photochemical reaction at the surface and could thus modify surface viscosity and hence elasticity of the surface film or adsorption at the surface.
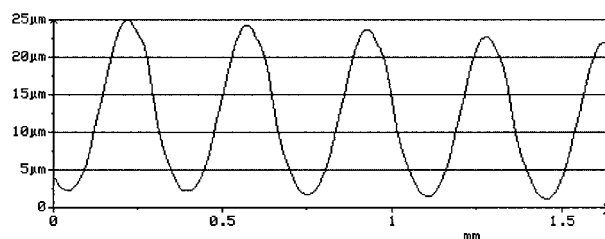


**Figure 8.** Sinusoidal type profile for cells.

## VI. Interpretation

It follows from the discussion that thickness of the sample is an important parameter with regard to the evaluation of surface deformation properties.[13] The speed at which the sample moves governs the surface viscosity because it modifies the photochemical reaction and hence the surface properties, as well as adsorption.

It is worthwhile to compare the two formulations for the same film thickness of, viz., 130 $\mu$m (cases A and B). In these two cases, where the speed of translation and the intensities of irradiation are identical, 20 and 40 $\mu$m high cells are observed for formulations I and II. This shows that the height of the relief is directly related to bulk viscosity of the film, as previously mentioned.[13]

For a given formulation, such as I, if the speed of sample displacement decreases from 40 to 25 m·min$^{-1}$, the dose of energy received increases from 50 to 65 mJ·cm$^{-2}$ ,and the for the same sample thickness of, viz. 140 $\mu$m, the chevron structure of the surface turns into a cell structure with a relief of 30 and 20 $\mu$m, respectively, as shown in Figures 3 and 4.

With a slower speed, i.e., a higher exposure time, the photochemical reaction will be favored, so that the surface of the film will become more cross-linked and of different composition owing to the chemical species: this case can be assimilated to a higher viscosity and to influence of adsorption. Accordingly it has been shown that the surface free energy increases when photo-cross-linking takes place,[16] and in that case, the term $(dT/d\Gamma)$ as given in expression 5 can be positive or negative, i.e., leading to turbulence or not. In fact, the formation of cells corresponds to a state that is further away from turbulence than the case of chevrons.

It would be worthwhile to look at a case where $(dT/d\Gamma)$ is negative: in that event the system would be damped, and no relief would appear. This has been observed with a displacement speed of 20 m·min$^{-1}$ (viz. a dose absorbed of 95 mJ·cm$^{-2}$).

Another interesting issue is the shape of the relief. With chevrons the profile is rather of the crenel type and even with two components, whereas, with cells, the profile is sinusoidal and of symmetrical shape as shown in Figures 7 and 8. This observation compares with the above-mentioned one with regard

to the appearance of cells, as far as stability or instability states are concerned. When working under static conditions of irradiation, without movement of the sample under the lamp, the results are identical for the surface deformation which appears.

As for the analysis using the above-mentioned elasticity Marangoni number, $E$, if the Schmidt number $S$ is high, i.e., for a high-viscosity $\nu$ and a low diffusion coefficient $D$, the system is damped. If this value is low, i.e., for low viscosity and a high diffusion coefficient, turbulence is possible. This can be substantiated by comparing on one hand the less viscous formulation I, leading to stars, chevrons, and a state of higher turbulence, and on the other hand, the more viscous formulation II, which leads to regular cells.

Such spatiotemporal structures can also be observed with nonlinear dynamical phenomena in chemical systems[17] as found in biology, and then chemical wave patterns appear.

## VII. Conclusion

The thermodynamics of irreversible processes applied to the surface deformation of photopolymerizable acrylate films permits one to explain unusual expected behaviors produced by UV irradiation. The succession of figures in going from cells to waves and stars pictures states of increasing instability. It is worthy of note that even nondeformed surfaces can be observed on irradiation with the formulations under study.

Bulk viscosity, adsorption, and diffusion coefficient of diffusing species provide a means for predicting the surface profile. The peculiar case investigated in the present study is an academic example illustrating the theoretical predictions established during the past two decades.

Many applications can be derived from these observations, especially in the field of microoptics.

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