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Self-organization in dry photopolymerized acrylate films
1. Irreversible thermodynamics analysis

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Abstract

Space and time instabilities can appear as very general phenomena at the surface of liquid or viscous films submitted to constraints. In the case of dry photopolymerized acrylate films, the surface relief at the monomer–polymer interface is examined within the framework of theories of irreversible process thermodynamics. A classical model as a function of time is adapted for linear behaviour for reaction and diffusion at the surface. This approach places the surface modification, irrespective of the medium in contact with the acrylate film, in a general thermodynamic sense of hydrodynamic instability, where marginal states are involved, and permits a prevision of the stability to be envisaged. A numerical application is proposed.

Keywords: Irreversible thermodynamics analysis; Photopolymerized acrylate films; Self-organization

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1. Introduction

Spatio-temporal structures associated with hydrodynamic instabilities are commonly observed in thin liquid or polymer films on evaporation or boiling of the liquid mixture [1–3]. They are characterized by deformation as waves or cells and by instabilities at the planar interface and result mainly from heat [1–3] or matter [1–9] transfer, but can also involve chemical reactions [6]. Evidence has been provided that such spontaneous interfacial deformations may only occur if the following necessary, but not sufficient, condition is fulfilled: the component diffusion goes from the liquid with lower diffusion coefficient to that exhibiting a higher value [4]. However, oscillatory instabilities with an overstable critical state may also be observed under suitable conditions in the case of diffusion from the phase with the higher diffusion coefficient to that with the lower value [5]. This reveals the large variety of situations involving hydrodynamic instabilities.

The thermodynamics of irreversible processes has been applied to the analysis of this behaviour [1–9]. The foundations of interfacial thermodynamics in the formation of these structures have been laid by Glansdorff and Prigogine [7]. The case of self-organizing systems displaying dissipative structures and spatial order through chemical reactions has been examined by Nicolis and Prigogine [10].

Some cases of instabilities and spatial patterns in association with photochemical reactions have been reported [11,12] on irradiation of the whole polymer surface or using a pulsed laser [13]; these were attributed to thermal side effects or diffusion processes. It is known that the competition between a chemical reaction and diffusion, or another hydrodynamic effect, in the bulk can lead to structure formation. In such cases, the effect results from the coupling between a chemical or physicochemical process and hydrodynamics. These observations apply to the dry photopolymerization of acrylate films, as observed recently.

The generation of relief has been observed during the photopolymerization of various acrylate films coated on glass substrates on illumination of the sensitive resin by a system of parallel fringes (obtained either by the interference of two laser beams or by using a mask of suitable amplitude) [14–17]. However, if the photopolymerizable material is sandwiched between two glass plates, so that no relief can arise at the interface, as in the research work carried out by Jost and Lougnot [18], a periodic distribution of optical properties appears inside the film [18–21] and results in the production of volume phase holograms. A similar behaviour has also been observed with acrylamide-based dry photopolymer films [22].

In all cases under consideration, a periodic structure formation of the polymer film has been observed, either at the surface or inside the medium. The results obtained by Jost

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[23] have clearly revealed the effect of competition between photopolymerization and monomer diffusion. This also applies to the open system where the film surface is free.

In this study, special attention is given to the effect of the coupling between photochemistry and diffusion at the film surface, and the possibility of hitting upon particular sets of parameters that may give rise to self-organization structures. This is a classical approach which relies on the thermodynamics of irreversible processes in systems that are out of equilibrium [1–10].

The study of relief formation or deformation at the surface of photopolymerized acrylate films should provide a means of determining the conditions which affect the appearance of spatial or spatial and temporal structures. The criteria of stability and instability should thus be defined in connection with the characteristics of the phases involved.

When concentration or temperature stresses occur at the surface of a liquid, waves can appear longitudinally and (or) transversally and, in addition, cells can form. Velarde and coworkers [8,9] have examined this problem.

Two approaches were used for the mathematical analysis of the surface structure, depending on the physical properties of the materials. The first considers the general behaviour of the system studied in terms of the stability criteria defined by Chu and Velarde [9]. Then, the spatial and temporal characteristics according to Hennenberg et al. [6], in a linear analysis, are compared with the experimental results. The non-linear approach suggested by Nicolis and Prigogine [10], although theoretically possible, is much more complicated.

2. Experimental details

This section summarizes the experimental results published elsewhere [18,23,24].

2.1. Sample preparation

1. As in the research work conducted by Jost and Lougnot [18,23], pentaerythritoltriacrylate (PETA) was used as the monomer and a benzoin derivative as the photoinitiator. The holographic irradiation was performed with a krypton laser at 356.4 nm with an interfringe Λ of 1 μm, i.e. 10^3 lines mm^{-1}. Irradiation from 2–10 s with an intensity of 0.2–4 mW cm^{-2} was applied. The polymer mixture with a dynamic viscosity of about 30 P was deposited as a film, 50 μm thick, between two glass plates.
2. As in the research work reported by Croutxé and Lougnot [24], a mixture of dipentaerythritol (DIPEPA) and another acrylate was used. A benzyldimethylketal (Irgacure 651, CIBA) was chosen as photoinitiator. The polymer mixture was deposited on a glass slide with a thickness of 50 μm. The irradiation was carried out through amplitude masks, with various interfringe distances, using a polychromatic UV lamp of 4 mW cm^{-2} intensity. The irradiation times were of the order of a few minutes, and a bleaching post-treatment was performed. The relief developed in the laboratory atmosphere. The experiments were carried out at room temperature and at 50 °C. The dynamic viscosity of the mixture was 30 P at 25 °C and 3.5 P at 50 °C. The available interfringes ranged from 200 to 25 μm, i.e. 5–40 lines mm^{-1}.

2.2. Optical analysis

The profiles of the generated reliefs were observed with an optical interference microscope and visualized on a computer screen which also provided hard copies of the files [24]. The details of these reliefs were analysed with a total magnification of 40×.

Typical examples are shown in Figs. 1 and 2 for the same acrylate formulation irradiated according to different procedures: 3 min of irradiation through a mask and 3 min of post-photopolymerization in the case of Fig. 1; 4 min of irradiation through a mask and 2 min of post-photopolymerization in the case of Fig. 2. In addition to the sinusoidal profile replicating the periodicity of the amplitude mask, some substructure (more visible in Fig. 2 than in Fig. 1) was observed. This structure was more pronounced at higher temperature (50 °C), with irradiation for 2.5 min, as shown in Fig. 3.

In the case of the volume holograms obtained between two glass plates, an analysis carried out using acoustic waves also revealed a periodic distribution between irradiated and non-irradiated zones [25].

All these observations suggest the existence of dissipative organized structures. Care was taken to avoid side effects due to parasitic interferences.

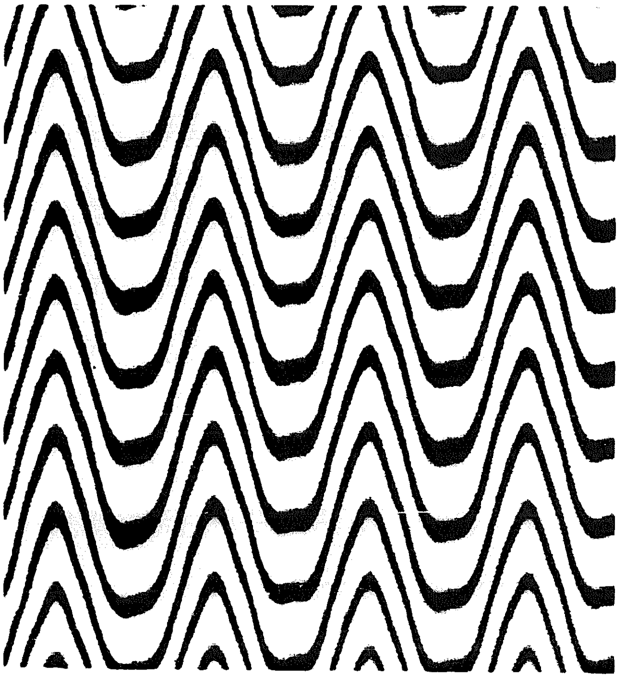

Fig. 1. Profile of a DIPEPA acrylate film after 3 min of irradiation at room temperature and $\Lambda = 50$ μm.

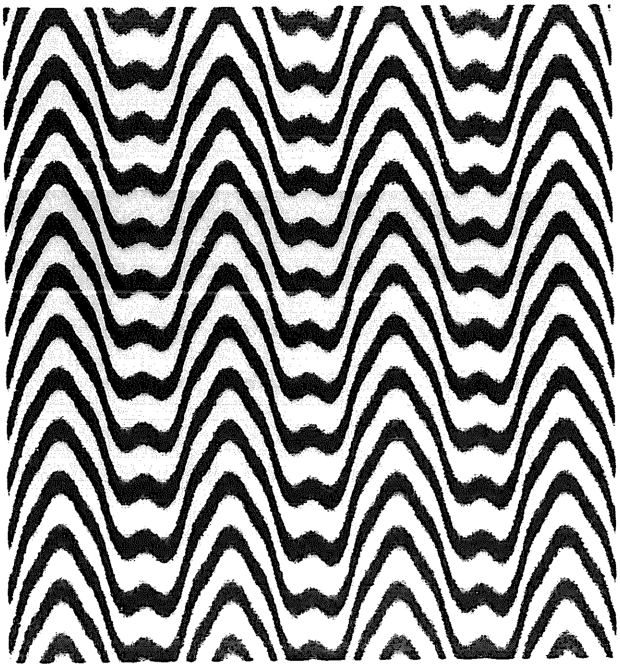

Fig. 2. Profile of a DIPEPA acrylate film after 4 min of irradiation at room temperature and $\Lambda = 50$ μm.

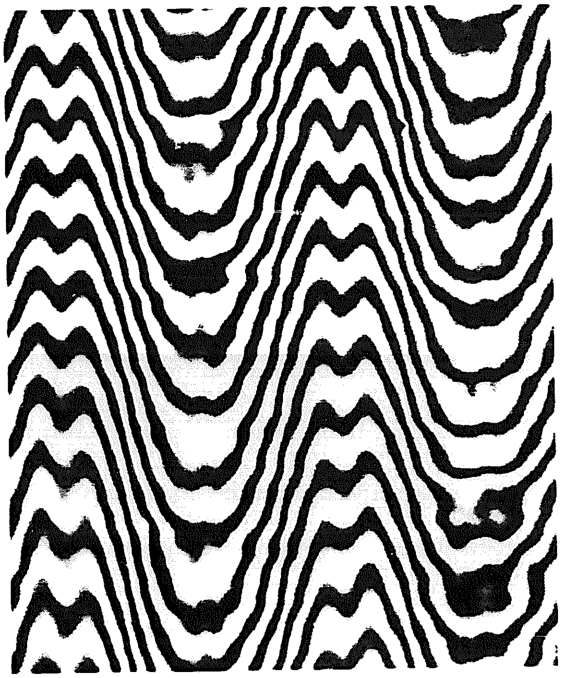

Fig. 3. Profile of a DIPEPA acrylate film after 2.5 min of irradiation at 50 °C and $\Lambda = 100$ μm.

3. Surface thermodynamics

Mass transfer deformation of an interfacial phase is a well-known problem in the theoretical approach of irreversible process thermodynamics. Various types of state, either stable or unstable, can appear. The marginal states found at the boundary between stable and unstable states are of particular interest and correspond to a latent situation.

Pearson [1] has given a theoretical hypothesis to account for the surface instability associated with temperature and concentration gradients and known as the Marangoni effect. This effect can be explained by longitudinal variations in the surface free energy, causing motions at the liquid surface, but also leading to forces which act on the liquid medium below the surface. Thus expansion takes place in regions of low interfacial free energy and contraction in regions of high interfacial free energy. Since no speed discontinuity can exist at the interface, fluxes come into being in in the liquids adjoining the surface: extension of the surface causes an increase in interfacial free energy and contraction a decrease. Two parameters have a particularly marked effect under these conditions: the concentration gradient at the interface, which is related to the initial difference in solute concentration, and the surface viscosity, which depends on the surfactants that are present at the surface. In this way, Marangoni-type strains usually lead to wave motions.

Sternling and Scriven [2] have investigated the effect of surface tension gradients resulting from longitudinal concentration variations, which induce hydrodynamic convection from the bulk phase. They have also observed surface deformation in association with matter convection [3].

A complete analysis of stability defines the conditions of stable and unstable domains and, in each, of oscillating and non-oscillating states. At the boundary between stable and unstable states, marginal states can appear. Peculiar instability states are usually defined as the critical marginal states leading to stable or unstable states:

- the neutral marginal stability state, when the system is stable and non-oscillating, but can become unstable under the effect of a fairly high strain;
- the overstable marginal stability state, when the system is oscillating around the stable state.

If the surface is thermodynamically unstable, longitudinal and simultaneous transverse waves can appear. Some simple rules have been established by Chu and Velarde [9] stating the necessary and sufficient conditions for the appearance of a stationary marginal state. Two dimensionless entities taking into account the diffusivity and the viscous properties are defined. In the case of a system consisting of two media (1 and 2) in contact, with medium 2 on top (as shown in Fig. 4), such that $\rho_2 < \rho_1$, if D_1 and D_2 are the respective diffusion coefficients of the species in these two media, N_D is given by the ratio

$$N_D = \frac{D_2}{D_1} \tag{1}$$

If ν_1 and ν_2 are the kinematic viscosities, N_ν is defined as

$$N_\nu = \frac{\nu_2}{\nu_1} \tag{2}$$

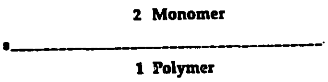

Fig. 4. Schematic representation of the interface between media 1 and 2.

Five different possibilities of overstable states, which can be related to different experimental behaviour, may appear:

1. if $N_D < 1$ and $N_\nu > 1$, there is no oscillatory solution;
2. if $N_D > 1$ and $N_\nu < 1$, there are longitudinal and transverse waves;
3. if $N_D < 1$ and $N_D > N_\nu$, the two types of wave are present;
4. if $N_D > 1$ and $N_\nu > 1$, but not far from unity, a transverse wave is present and the longitudinal wave is affected;
5. if $N_D > 1$ and $N_\nu > 1$, but very different from unity, only a transverse wave is produced.

If these criteria are applied to our experimental observations, predictions can be made.

If medium 2 is the monomer remaining at the surface, due to the inhibiting effect of oxygen on the photopolymerization reaction [26], and medium 1 is the polymer, the diffusion coefficient D_2 is greater than D_1, and N_D is greater than unity. The viscosity of the monomer mixture is 30 P and that of the polymer at the start of the crosslinking process is higher, so that N_ν is lower than unity. Therefore the system corresponds to case (2) with the possibility of longitudinal and transverse waves in a marginal stability state. Accordingly, the system is usually stable, but may become unstable, even under the effect of a low constraint.

In the case of a system sandwiched between two glass plates, the same criteria apply at the 2–1 monomer–polymer interface in the bulk of the film. In contact with the glass, N_D is lower than unity, glass being medium 2, and N_ν is higher than unity. In this case, corresponding to case (1), no oscillatory structure can appear. Thus instabilities can only be expected at the monomer–polymer interface.

This very simple rule permits the existence of dissipative structures and instabilities to be predicted in the photopolymerization of multifunctional acrylate films.

4. Linear theoretical model and results

In the 1970s, many attempts were made to suggest equations for interfacial motion. That introduced by Hennenberg and coworkers [4–6] is particularly interesting, since it provides a means in linear analysis to account for both reaction and diffusion at the interface [6] and considers the stability of a planar interface where matter transfer and chemical reactions take place simultaneously. A linear analysis of the perturbations in such a situation has been developed by Hennenberg et al. [6] for an interface treated as a bidimensional newtonian fluid. The coupling of the surface reaction and matter transfer with the hydrodynamics of the liquid viscous medium was examined.

4.1. Theoretical model [6]

In a first approximation, the fluxes are assumed to be proportional to the forces in a system out of equilibrium where $\rho_1 > \rho_2$. This could be the case at the beginning of the photopolymerization reaction, for example.

The main difference at the surfaces of the two systems is mainly due to the higher oxygen concentration at the free surface (in the case of research work conducted by Croutxé and Lougnot [24]), because oxygen has an inhibiting effect on the photopolymerization, as demonstrated in Ref. [26].

According to the general linear equations established in Ref. [6] for a planar interface, where chemical reactions and matter transfer can occur, the local variation in adsorption Γ_γ is assumed to be due to exchanges with the volume phases, the chemical reactions at the surface, the convection at the surface and the diffusion at the surface. The variation in the concentration of constituent γ at the surface s may be written as

$$\delta_t \Gamma_\gamma = F_\gamma\{\Gamma_\beta\} + J_\gamma + D_\gamma^{s} \nabla_s^2 \Gamma_\gamma - \mathrm{div}^{s} \nu_s \Gamma_\gamma \qquad (3)$$

where $F_\gamma\{\Gamma_\gamma\}$ is the source of γ produced by chemical reactions, J_γ is the flux resulting from exchanges with the volume phases, D_γ is the diffusion coefficient at the surface and ν_s is the mean speed at the surface. The geometric surface variation is considered to be negligible. If the system is infinite in the x and y directions, but limited in the z direction, the solution for all spatial and temporal perturbations of quantity Q may be written as follows

$$\delta Q(x,y,z,t) = \int_{-\infty}^{+\infty} \mathrm{d}k_x \int_{-\infty}^{+\infty} \mathrm{d}k_y \, \mathrm{e}^{\mathrm{i}(k_x x + k_y y) + nt} \delta Q_h(z) \qquad (4)$$

where k, the wavenumber corresponding to spatial deformation, is defined as

$$k = \sqrt{k_x^2 + k_y^2} \qquad (5)$$

and n is a real or imaginary number characteristic of the temporal variation.

Number n, which may be written as follows

$$n = n_r + \mathrm{i} n_i \qquad (6)$$

with a real and an imaginary part, can represent different situations:

- if n is real and positive, the fluctuation increases and instability can appear for a critical value;
- if n is real and negative, the system is stable;
- if n is imaginary and different from zero, the system oscillates as a function of time.

Marginal states are characterized by zero value for the real part of n. If both the real and imaginary parts of n are zero, the situation corresponds to the "neutral" marginal state, a "latent" stable state which may become unstable.

The "overstable" marginal state corresponds to a zero real part of n and an imaginary part different from zero: the system oscillates around the stability state.

In order to simplify the problem, if only one chemical variable is involved at the interface, the dispersion equation can be solved and the solution n for the time dependence can be calculated [6].

When Γ_T is the total surface adsorption, ρ_1 and ρ_2 are the densities of the media, ϵ and χ are the surface shear and dilatation viscosities respectively and μ_1 and μ_2 are the bulk dynamic viscosities, C is defined as follows

$$C_{\gamma\beta}=\left(\frac{\mathrm{d}F_\gamma}{\mathrm{d}T_\beta}\right)+\left(\frac{\mathrm{d}J_\gamma}{\mathrm{d}T_\beta}\right) \tag{7}$$

where flows due to chemical reactions (F) and diffusion (J) at the surface are involved if constituents β and γ are present. C has the dimensions of the inverse of time.

If the problem is restricted to only a longitudinal wave in a direction parallel to the x axis, the wavenumber k is taken to be equal to k_x and corresponds to the interfringe Λ

$$k=\frac{2\pi}{\Lambda} \tag{8}$$

Our attention is mainly focused on the temporal evolution which can be deduced from Eq. (4).

Two cases to calculate solution n were conceived.

In the first case, where

$$k^2\leq\frac{n^2\left(\Gamma_\mathrm{T}+\frac{1}{2}\frac{\rho_1+\rho_2}{k}\right)}{(\Sigma+X)\,|(k^2D_\mathrm{s}-C)|} \tag{9}$$

n may be written as

$$n=\frac{\pi_2^{(k)}-\pi_3^{(k)}}{2}\pm\frac{1}{2}(\pi_2^{(k)}+\pi_3^{(k)})\sqrt{1-4p} \tag{10}$$

with

$$p=\frac{\pi_1^{(k)2}}{(\pi_2^{(k)}+\pi_3^{(k)})^2} \tag{11}$$

$$\pi_1^{(k)}=\frac{\alpha\Gamma k^3}{k\Gamma_\mathrm{T}+\rho^*}\text{ with }\rho^*=\frac{\rho_1+\rho_2}{2} \tag{12}$$

$$\pi_2^{(k)}=C-k^2D_\mathrm{s} \tag{13}$$

$$\pi_3^{(k)}=\frac{k^3(\Sigma+X)+4\mu^*k^2}{k\Gamma_\mathrm{T}+\rho^*}\text{ with }\mu^*=\frac{\mu_1+\mu_2}{2} \tag{14}$$

Parameter α is defined by the relationship

$$\delta\sigma=-\Sigma\alpha_\gamma\delta\Gamma_\gamma \tag{15}$$

between the surface free energy σ and the adsorption Γ_γ for a given constituent γ.

Of the different criteria suggested in Ref. [6], the following simple criterion is first recommended:
if $C-k^2D_\mathrm{s}\leq 0$, the system is stable;
if $C-k^2D_\mathrm{s}>0$, the system is unstable.

In the marginal state with exchange of stability, according to Ref. [6]

$$C-k^2D_\mathrm{s}=\frac{\alpha\Gamma k}{k(\Sigma+X)+2(\mu_1+\mu_2)} \tag{16}$$

which shows the effect of the surface and bulk viscosities and the tensioactivity.

Table 1
Values of the different parameters involved in Eq. (9) (SI units)

Parameter	PETA system	DIPEPA system
μ_1	9 Pl (90 P)	9 (Pl) kg m^{-1} s^{-1}
μ_2	3 Pl	3 Pl
k	6.3×10^6 m^{-1}	1.25×10^5 m^{-1}
k^2	4.0×10^{13} m^{-2}	1.56×10^{10} m^{-2}
k^3	2.5×10^{20} m^{-3}	1.95×10^{15} m^{-3}
D	10^{-14} m^2 s^{-1}	10^{-15} m^2 s^{-1}
$\Sigma+X$	0.02 kg s^{-1}	10^{-4} kg s^{-1}
ρ_1	1.1×10^3 kg m^{-3}	1.1×10^3 kg m^{-3}
ρ_2	9×10^2 kg m^{-3}	9×10^2 kg m^{-3}
Γ	10^{-2} kg m^{-2}	1 kg m^{-2}
Γ_T	2×10^{-2} kg m^{-2}	2 kg m^{-2}
α	10^4 m^2 s^{-2}	10^4 m^2 s^{-2}
C	10^{-1} s^{-1}	10^{-1} s^{-1}
n'	0	$-1.14\times10^6+i8.75\times10^6$
n''	-4×10^{13}	$-1.14\times10^6-i8.75\times10^6$

In the second case, where

$$k^2\gg\frac{n^2\left(\Gamma_\mathrm{T}+\frac{1}{2}\frac{\rho_1+\rho_2}{k}\right)}{(\Sigma+X)\,|(k^2D_\mathrm{s}-C)|} \tag{17}$$

the solution n is real, but instabilities can appear under certain conditions [6] and only if $|C|>k^2D_\mathrm{s}$: such a condition is close to the previous one. This approach completes the preceding one, thus permitting generalization to all cases. According to Ref. [6], n can be calculated by

$$n=-\frac{(k^2D_\mathrm{s}-C)[k^2(\Sigma+X)+2(\mu_1+\mu_2)k]+\alpha\Gamma k^2}{\left(\Gamma_\mathrm{T}+\frac{1}{2}\frac{\rho_1+\rho_2}{k}\right)(k^2D_\mathrm{s}-C)+k^2(\Sigma+X)+2(\mu_1+\mu_2)k} \tag{18}$$

This can correspond to the case of system (2).

4.2. Numerical application

The n values have been calculated for both systems (1) and (2), as described previously. The values of the different parameters used for the calculations are shown in Table 1. Medium 1 is the polymer and medium 2 is the monomer. A lower value was taken for the surface viscosity in the case of the DIPEPA system which is open to air, because of the presence of oxygen at the monomer mixture surface, which inhibits polymerization [26].

Depending on the sign of inequalities (9) and (17) and assuming that the systems obey the first case described in Eq. (9), as verified by the above-mentioned simple rule, the two systems described in Refs. [23] and [24] were considered. They have the same bulk properties and differ only in the spatial frequency, surface viscosity and adsorption. Expression $C-k^2D_\mathrm{s}$ was found to be negative for Jost's system [23], thus warranting the prediction that it may be fairly stable.

However, this value was positive or negative for the system of Croutxé and Lougnot [24] which, for a diffusion constant $D = 10^{-15}$ m^2 s^{-1}, may be unstable, but more stable for a diffusion coefficient of 10^{-10} m^2 s^{-1}.

Jost's system [23], taking into account the number of lines per millimetre in the hologram and the measured diffusion constant D_s, is of the first case type. The stability at the monomer–polymer interface seems to be favoured in a first analysis, because of the higher value of k which leads to a negative value of $C - k^2D_s$. For the results reported in Ref. [23], n has been found to take a zero or negative value, the system is stable and no oscillations are expected, as observed experimentally. Therefore the system is either in a marginal state of stability or is stable, all fluctuations being damped.

In the case of Ref. [24], n is found to be negative with an imaginary part which indicates that the system, although stable, can oscillate.

According to Ref. [6], for $p > 1/4$, there is a complex solution with temporal oscillations, whereas with $p < 1/4$, a real solution is obtained and no temporal oscillations are observed. Calculations made using the data given in Table 1 lead to a p value of 10^{-8} for Ref. [23], so that the system is stable. In the case of the open surface [24], p reaches a value of 15 and oscillations may appear. These calculations and predictions are in good agreement with the experimental observations. In the case of the open surface, oscillations appear (as shown in Figs. 1 and 2) for the room temperature results, which are more pronounced at a temperature of 50 °C (Fig. 3).

Therefore the linear analysis of the stability according to Hennenberg et al. [6] predicts that more possibilities of behaviour are offered by the open system, which is in agreement with our experiments. Recently, the influence of the surface adsorption on the surface viscosity has been examined and differences in the relief height and kinetics of formation have been observed. Selected samples of acrylates also lead to the formation of hexagonal cells after photopolymerization. This is described in Part 2 of this paper.

4.3. Comments

From the experimental values given in Table 1, the simplified criterion $C - k^2D_s > 0$ allows predictions to be made of the instabilities. However, the interest in the linear approach described in Ref. [6] is concerned with the fact that different contributions (and not only the Marangoni effect) were taken into account. In addition, it must be kept in mind that parameter C is not easily measurable in the present case, and can only be estimated.

This simple example shows the many possibilities offered by changing important parameters, such as the interfringe Λ, the diffusion coefficient or the surface viscosity. Studies are underway in order to differentiate between the effects of these various parameters.

This first linear analysis shows that it is possible to establish stable and unstable regimes during the formation of dry photopolymer films and describes the main effective parameters which can be varied in the experimental study. Nevertheless, the characteristics of the system can be such that the oscillation or instability cannot be observed during the laboratory experiment, e.g. because the wavelength of the perturbation is too high or the amplification factor is too low.

The results reported in this paper complement various observations on photochemical reactions perturbed by convective motions [11–13].

Booth [27] has reported the diffraction efficiency as a function of the exposure time, power density and readout wavelength, corresponding to the so-called overmodulation governed by Kogelnik's theory [28]. The complexity of these observations may perhaps be related to the existence of spatial and temporal dissipative structures.

Surface structures have been observed for pulsed UV laser irradiation of polymer fibres (e.g. polyamide or polyethyleneterephthalate) [13,29]. These modifications have been attributed to surface melting and Marangoni convection and shrinkage effects.

Most recently, papers have been contributed on the mechanism of phase rebuilding due to photoreactions on polymer surfaces without micromelting. Uniform nanostructures have been observed at the surface of anthracene by atomic force microscopy (AFM) [30] and have been related to the molecular packing of the crystals. In all cases, spatial restructuring of the surface has been observed [31]. This phase rebuilding mechanism is very recent and supports our observations in photopolymerization.

A non-linear approach, taking into account the coupling of chemical reactions and diffusion, would describe the behaviour of such media more accurately, especially for the volume holograms. However, the mathematical analysis of the corresponding system of equations would not be feasible, making this first simplistic approach more attractive.

5. Conclusions

The photopolymerization of acrylate films has shown that, on spatially controlled irradiation, structure formation at the film free surface, and even inside the film, can take place. The dissipative structures can be analysed in a first approach by using, in a linear method, the thermodynamics of irreversible processes. According to Hennenberg et al. [6], some simple criteria of stability can be proposed to take into account the fluxes, diffusion coefficients and spatial periodicity of the irradiation.

Self-organization structures are characteristic of associated diffusion, gradients of surface energy or chemical reactions. Microscopic observation of the spatial distribution of relief has revealed that this phenomenon seems to be of a general type in the case of photopolymerization.

Studies are still in progress to examine more thoroughly the effect of the main parameters in dissipative structures. As concluded by Jost [23] and Croutxé and Lougnot [24], diffusion seems to be the most important parameter in this reaction–diffusion coupling behaviour. Conversely, it is also worthy of note that this mechanism can generate chemical instability [6], which should be taken into account in the kinetic evolution of the photopolymerization process. This makes it possible to explain some experimental anomalies observed in our laboratory, e.g. the time dependence of the diffraction efficiency is either monotonic (thus leading to a stable value) or oscillatory. The appearance of relief at the free surface of acrylate photopolymerized films can be accounted for, and the evolution of the relief height by changing only the surface composition shows clearly the critical influence of the surface properties in the self-development of acrylate films.

It seems that the thermodynamic approach is well suited to the explanation of many facts observed in photopolymerization, and may help to obtain a better understanding and control of the surface and interface transformation phenomena.

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