

Thermodynamics of Surface Self-Developing Structure Formation on Polyamide Films under Ultraviolet Irradiation

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ABSTRACT: Polyamide terpolymer films can be obtained by the evaporation of a solvent–terpolymer–photoinitiator mixture on a glass plate. Through ultraviolet (UV) irradiation, self-developing properties are observed. The nuclear magnetic resonance (NMR) study of the photochemical reaction involved in such a process permits us to propose a mechanism with a diffusion of solvent in the irradiated areas. The thermodynamics of irreversible process have been applied to the analysis of such a system behavior, and an analysis of the stability of the system resulting from its residual solvent content has been made. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 645–653, 2002

Key words: self-developing; polyamide; thermodynamics; irreversible process; ultraviolet irradiation film.

INTRODUCTION

Photopolymers belong to a recently proposed class of materials for application in the optical field.^{1–4} Under ultraviolet (UV) irradiation, self-developing materials allow us to obtain locally modified properties either by modification of the height of the relief and/or of the refractive index in the irradiated area.

Viscous mixtures of acrylates can be photopolymerized in the presence of a photoinitiator,^{1–3} but there is a need for more polymers that are more easy to handle. The basic idea of this work is the engineering of a polymer, working as a solid film, self-developing, transparent after irradiation, and with an optical performance similar to that of the acrylates or other photoresists.^{4–6}

Polyamides seem to exhibit interesting properties, such as a high melting temperature (220°C) and a high water adsorption release.⁷ The photosensitive properties of the polyamides seemed interesting because of the numerous possibilities of photodegradation and photo-cross-linking under UV irradiation, which would also induce a refractive index modification. Polyamides are very sensitive to light irradiation; the main effects are chain cleavage, cross linking, and yellowing of the polymers.^{8–10} We primarily observed photodegradation and photooxidative degradation of heterochains, leading to lower mechanical strength. Polyaramides have also interesting photosensitive properties^{11,12} with chain cleavage and formation of oxidized groups.

Exploiting these properties was a matter of interest in the preparation of self-developed structures by irradiating the sample through a lined glass mask according to the usual experimental procedures, as first used in experiments

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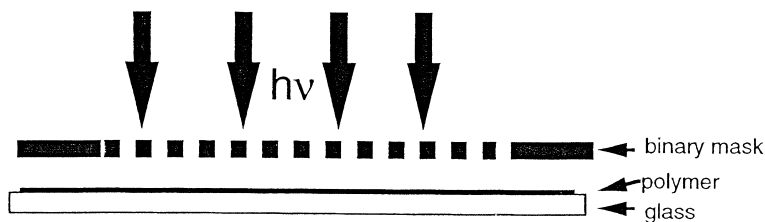


Figure 1 Experimental device for ultraviolet irradiation.

with acrylate films. The interest of such studies is connected with the possibility of using polyamides for information storage, as the cross linking produced by irradiation is highly favorable for modification of the refractive index. Polyamides can so be used as photopolymers owing to their transparency, absence of odor, and formation of a relief under UV irradiation. The formation of a relief is associated with a modification of the refractive index, as observed,¹³ and the profile varies with the irradiation conditions.

Irreversible process thermodynamics can be successfully applied to the analysis of the relief formation^{14–17} under spatially controlled UV irradiation. The aim of this work is to precisely explicit the thermodynamics of the formation of the relief.

EXPERIMENTAL

Sample Preparation

A formulation contains 1 part polyamide-6 terpolymer Selar (Du Pont); 0.4 parts benzoine ether, which is the photoinitiator; and 10 parts solvent, which is a chlorinated alcohol (Aldrich). The terpolymer contains also aromatic groups and has a mean molecular weight of $M_w = 30,000$. The dissolution of the terpolymer is obtained by ultrasonication of a mixture of solvent and photoinitiator. A thin film of nearly $73 \mu\text{m}$ is obtained by spreading the collodion on a glass plate with a doctor-knife blade. A film of nearly $13 \mu\text{m}$ in thickness is obtained after drying the film 20 h in an ordinary atmosphere. The solvent weight loss attains 83.5% at the maximum, but intermediate solvent contents can be observed. The drying condition is a very important parameter in this case.

Irradiation Conditions

Optical diffractive elements are formed under a 15-min irradiation with a UV lamp through a

lined glass mask by maintaining the glass plates at a temperature of 53°C with the help of a warming plate. The UV lamp (HBO 350W) is a high-pressure mercury vapor lamp that emits radiation with wavelength between 310 and 380 nm, with a mean power of 25 mW/cm^2 .

The glass mask is a binary amplitude mask with 20 lines/mm. The binary mask presents chromated lines. A constant distance between the mask and the film is maintained. The irradiation device is schematized in Figure 1.

Regular parallel waves are observed on the surface of the film, as shown in Figure 2, in an example for a glass mask with 20 lines/mm. A slight yellowing appears because of the photochemical reaction in the irradiated areas.

Profile Measurement

An optical profilometer from UBM Messtechnik GMBH is used. A laser beam of 780 nm in wavelength is focused on the surface of the sample and is reflected. The optical system moves so as to always focus the light on the surface. It is thus possible to obtain two-dimensional profiles, usually with a resolution of 1000 points/mm in the two directions of analysis and also three-dimensional images. The precision on the height measurements is $\pm 10 \text{ nm}$. A typical example is given in Figure 3: For a sample corresponding to an 81.6% loss of solvent, the relief height is on the order of 1000 nm. The profiles are usually sinusoidal, but they can be unique or double.

RESULTS

Influence of the Solvent Content

Depending on the preparation conditions, it appears that the form and height of the relief profile obtained after irradiation through a lined mask is also a function of the mass loss after drying of the film.

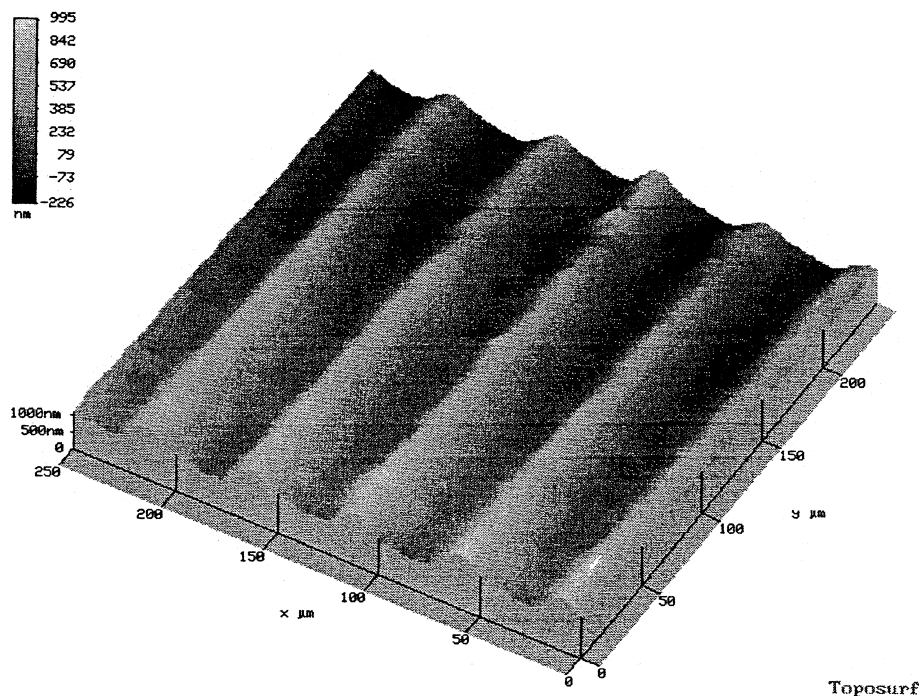


Figure 2 Three-dimensional representation of an ultraviolet-irradiated polyamide film through a mask with 20 lines/mm.

In Figure 4, the profile height is given as a function of the solvent mass loss after drying. It is noticeable that the mass loss is usually between 80% and 83.5%.¹³ In such conditions, the height can vary between 200 and 1200 nm in a sensitive manner. Weight losses are given in Table I. The form of the profile is also dependent on the solvent content. In the first part of the curve, peaks are symmetrical, but irregularities can appear in the lower part. Then regular peaks with symmetrical shape are observed, after which are seen peaks with a hollow at the top, double regular peaks, and then irregular peaks, and finally, totally irregular profiles appear. These different shapes are shown in Figure 5a to 5i for a decreasing

solvent content in the sample and for an irradiation time of 15 minutes through a mask with 20 lines/mm.

As the solvent content decreases, the profile becomes less symmetrical until an irregular shape is observed for the lower solvent content, as shown in Figure 5i, corresponding to a 83.5% weight loss. In that case, the viscosity of the polyamide film is the highest, so all displacements in the film were lowered. This observation is of utmost importance for the reproducibility: It appears that in ultimate cases, the profile height is variable along the surface without a strict correlation with the irradiation spatial frequency.

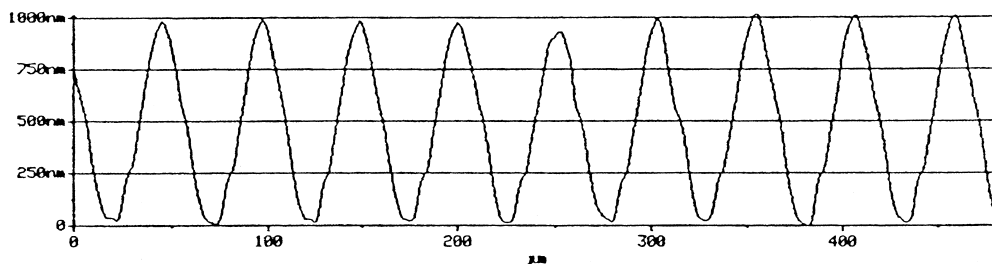


Figure 3 Profile after ultraviolet irradiation on a sample with a 81.6% weight loss after drying.

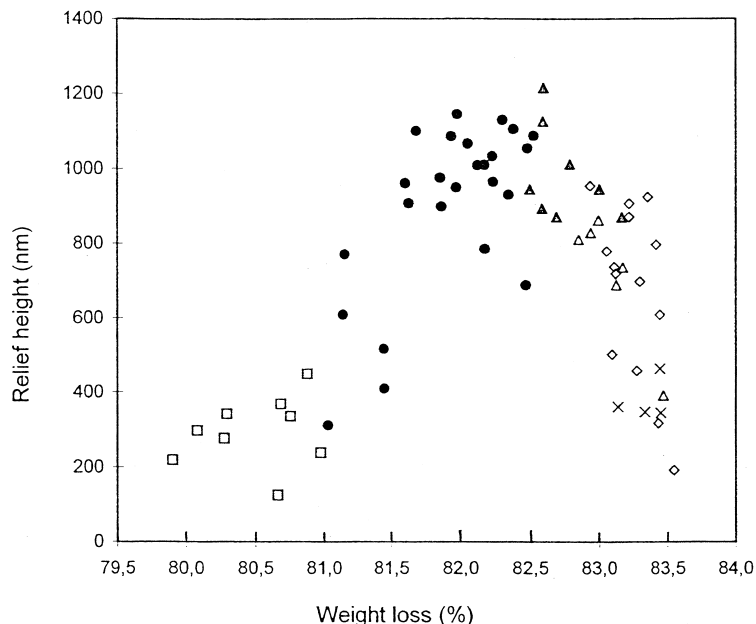


Figure 4 Evolution of the form and height of the relief obtained after irradiation through a mask with 20 lines/mm as a function of mass loss experienced during drying.

The Photochemical Reaction Involved

An NMR study of the photochemical reaction in the polyamide collodion was performed. An intense and fixed magnetic field and another weaker and variable field, perpendicular to the main field, are applied. ^{13}C NMR MAS (magic-angle spinning) has been used. High-speed rotation around the axis is performed so that the magic angle has a value of $54^{\circ}44'$. For a higher sensitivity, the Crossed Polarization (CP)-MAS NMR is used. In this method, there is a heteronuclear dipole interaction (^1H - ^{13}C or ^1H - ^{15}N), and a part of the proton magnetization is transferred to the rare spin nuclei.

Table I Solvent Weight Loss Percentage for Different Surface Relief Heights

Relief Height (nm)	Weight Loss (%)
200	80 ± 0.10
330	80.75
400	81.45
1200	82.60
900	83.22
450	83.44
200	83.55

In the terpolymer, before irradiation, the results show the presence of an important quantity of aromatic carbons corresponding to peaks at 128 and 136 ppm. The presence of the photoinitiator leads to peaks with a chemical displacement at 20, 30, 41, 77, 86, 129, 134, 135, 137, and 198 ppm, and the solvent leads to peaks at 77 and 101 ppm, as shown in Figure 6. In the case of the used solvent, the peak at 77 ppm is particularly large at its base, indicating that some of the solvent molecules have a strong interaction between their hydroxyl function and the rigid structure of the polymer.

For the irradiated sample shown in Figure 7, either the initiator peaks have disappeared or there is an enlargement of the peak base. This traduces both the immobilization of the functions in the material and the disappearance of some functions after the photochemical reaction.

Considering the ^{13}C NMR spectra, it is clear that the photoinitiator present in the photosensitive material before irradiation has no interaction with the macromolecular chains and disappears after UV irradiation. However, the fixation of some aromatic cycle groups issued from the initiator photocission to the macromolecular chains is a possibility.

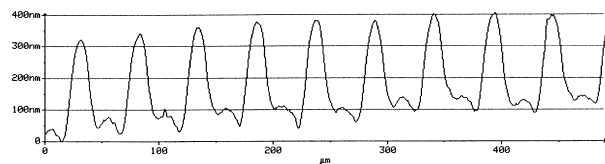


Figure 5a

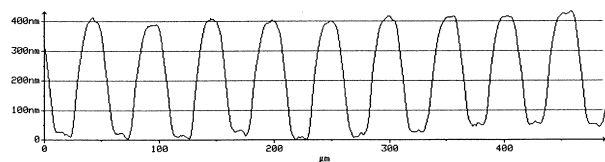


Figure 5b

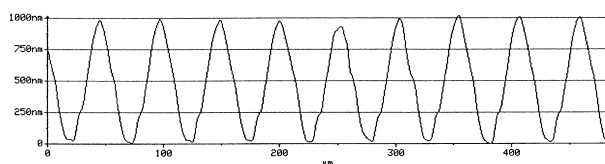


Figure 5c

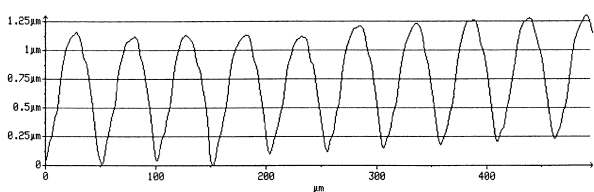


Figure 5d

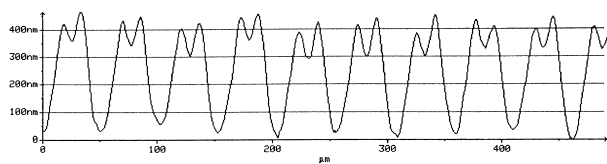


Figure 5e

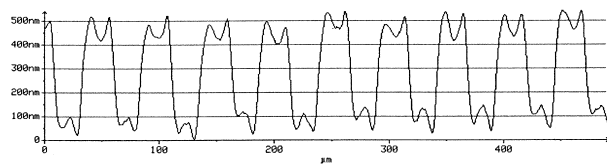


Figure 5f

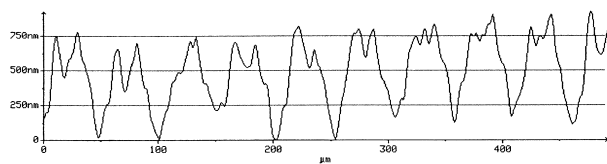


Figure 5g

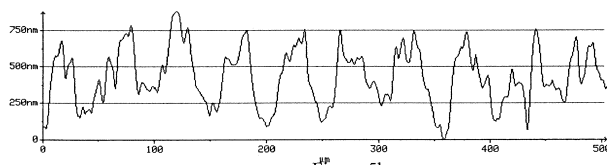


Figure 5h

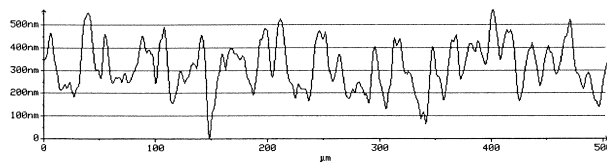


Figure 5i

Figure 5 Various profiles of the relief as a function of decreasing solvent content after drying the collodion, using the following weight loss percentages: 5a, 80.3%; 5b, 80.7%; 5c, 81.6%; 5d, 62.6%; 5e, 83.5%; 5f, 83.3%; 5g, 83.3%; 5h, 83.2%; 5i, 83.5%.

^{13}C and ^{15}N NMR studies show the presence of aliphatic amide functions in the polymer. The obtained NMR spectra clearly indicate that the solvent molecules' proportion leading to hydrogen bonds with the macromolecules increases after irradiation; thus, the affinity of the polymer chains for the solvent would be more important in the irradiated film than in the nonirradiated film. For the UV-irradiated sample, it seems that groups issued from the photoinitiator decomposition and containing aromatic cycles are also grafted on the polymer chains.

Thermodynamics of Irreversible Processes

It is well established that surface deformations appear when there is a gradient of composition

or of surface free energy.¹⁵⁻¹⁷ In the general case of the reaction-diffusion coupling the theoretical equations are known, and the stability of a plane interface from the mechanical—as well as from the chemical—point of view has been examined by Hennenberg et al.¹⁶ A linear analysis of interfacial chemical reactions and matter transfer stability has been made: The stability domains and the existence of marginal states have been established in the general case. Such an analysis has already been applied both to the case of acrylate films¹⁴⁻¹⁵ irradiated through a lined glass mask and even to samples entirely irradiated;¹⁷ the structures can then go from waves to hexagonal cells or isolated surelevated points. The different viscosities in the

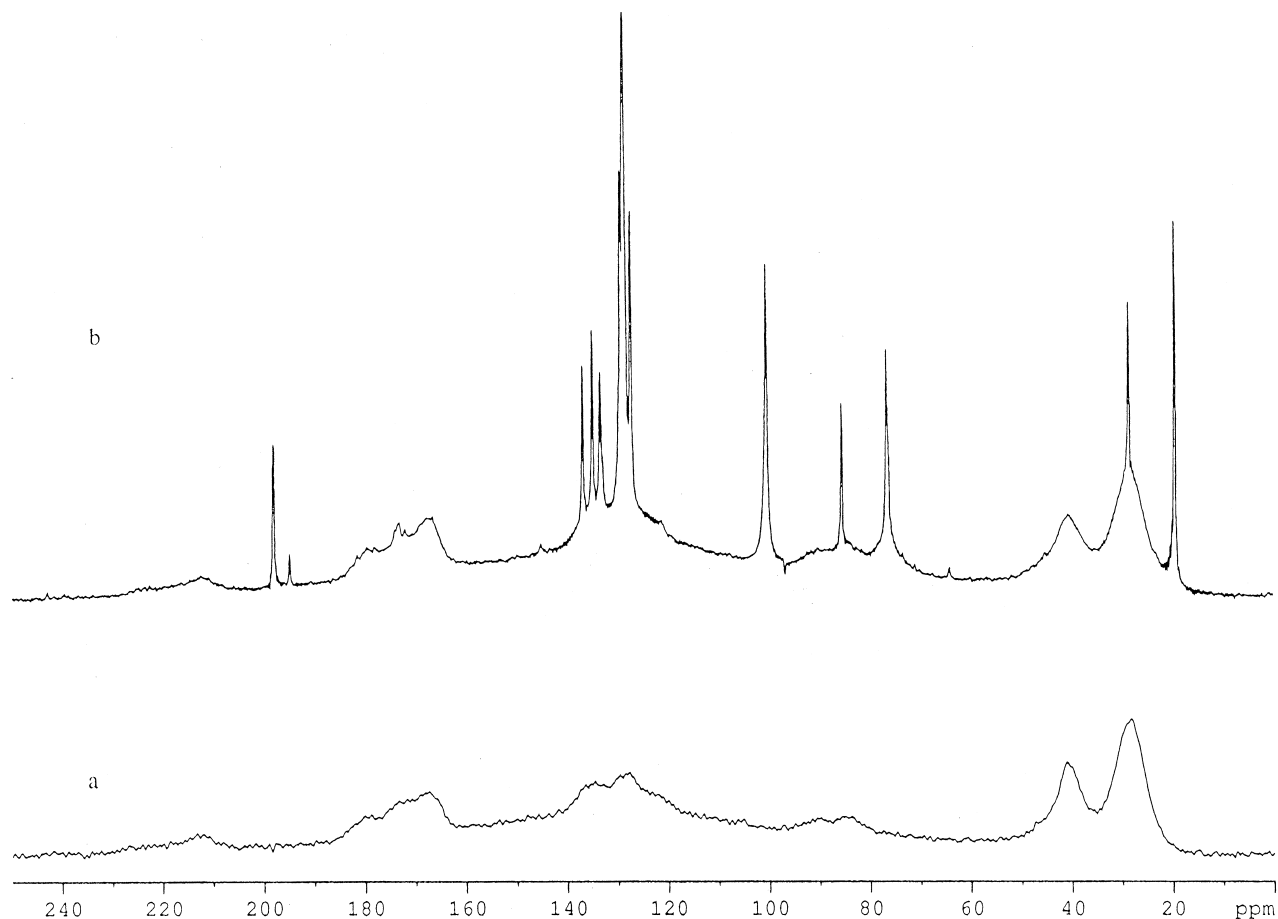


Figure 6 ^{13}C -NMR (nuclear magnetic resonance) MAS (magic-angle spinning) spectra for the nonirradiated polyamide sample formulation: a = terpolymer, b = nonirradiated formulation.

bulk of the mass as at the surface also have such an important role.¹⁷

Theoretical Equations

Surface Hydrodynamic Deformation

According to Hennenberg et al.,¹⁶ and as proposed in Lavielle et al.,¹⁴ the concentration variation of constituent γ at the surface s can be written

$$\delta_t \Gamma_\gamma = F_\gamma \{ \Gamma_\beta \} + J_\gamma + D_\gamma^s \nabla_\gamma^2 \Gamma_\gamma - \text{div}^s \nu_s \Gamma_\gamma, \quad (1)$$

with $F_\gamma \{ \Gamma_\beta \}$ being the source of γ produced by chemical reactions, J_γ the flux caused by exchanges with the volume phases, D_γ^s the diffusion at the surface, and ν_s the mean surface speed. Admitting the deformation as a perturbation on the surface, for a system infinite in x and y directions and limited in the z direction, the solution

for all spatiotemporal perturbed entities of Q is written as

$$\delta Q(x, y, z, t) = \int dk_x \int dk_y e^{i(k_x x + k_y y) + nt} \delta Q_k(z), \quad (2)$$

with k being the wave number corresponding to spatial deformation defined by

$$k = \sqrt{k_x^2 + k_y^2}, \quad (3)$$

with n being a number (real or imaginary) characteristic of the temporal variation.

The influence of other properties like adsorption must be elucidated. Moreover, the solvent content is a parameter modifying the local viscos-

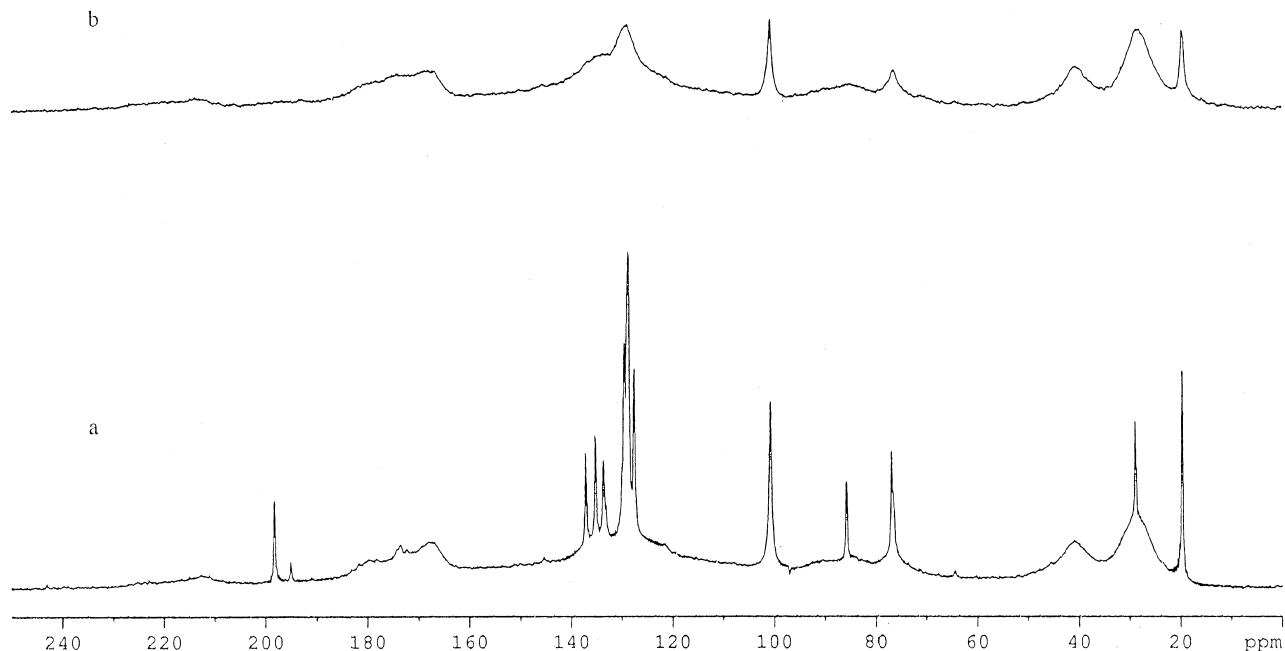


Figure 7 ^{13}C -NMR (nuclear magnetic resonance) MAS (magic-angle spinning) spectra for the irradiated polyamide collodion sample: a = nonirradiated formulation, b = irradiated formulation.

ity and the surface free energy. So between irradiated and nonirradiated areas, there is a gradient of surface free energy that is favorable to hydrodynamic effects with the appearance of a relief. The photochemical reaction can also lead to a volume modification by crosslinking in the irradiated area. So by combining the solvent diffusion horizontally and vertically and the contraction of volume and the hydrodynamic effects at the surface, conditions are gathered for the formation of a valley with a superimposed relief in the irradiated areas. The reaction–diffusion coupling plays also a role.

Two conditions can be proposed for such a system, where reaction and diffusion intervene in a coupled way. First, if the kinetics coupled with the diffusion stabilize the system, it is said that

$$C - k^2 D_s < 0, \quad (4)$$

and the solutions are always stable where

$$C = (dF/d\Gamma_\beta) + (dJ/d\Gamma_\beta), \quad (5)$$

F and J are the fluxes resulting from chemical reactions and the diffusion of species γ , Γ is the

adsorption of species β , γ could be the monomer, and β could be the solvent, for example.

k is the wave number

$$D_s \text{ the diffusion constant} \quad (6)$$

if to the contrary, there is destabilization, then

$$C - k^2 D_s > 0, \quad (7)$$

and there can be instability.

A representation is proposed under the form of a stability diagram, as shown in Figure 8. For the analysis of the stability, a diagram is proposed, representing the viscous term b as a function of the reaction–diffusion term a with

$$a = (C - k^2 D_s) / \sqrt{\alpha \Gamma k^3 / k \Gamma_T + \rho^*}; \quad (8)$$

$$b = \{[k^3(\varepsilon + \chi) + 4\mu^* k^2] / k \Gamma_T + \rho^*\} / \sqrt{\alpha \Gamma k^3 / k \Gamma_T + \rho^*}, \quad (9)$$

where α is the proportionality coefficient for the surface free energy σ to the adsorption Γ of species γ :

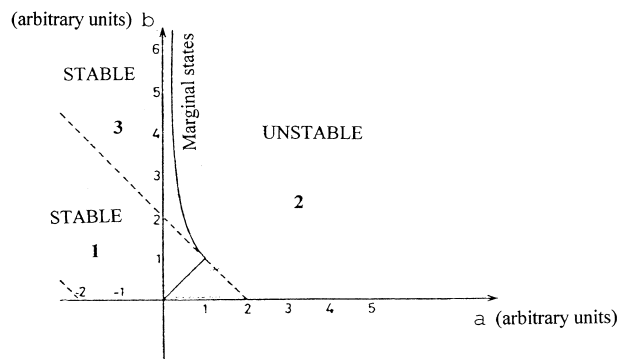


Figure 8 Stability diagram.

$$d\sigma = -\sum \alpha_\gamma \delta \Gamma_\gamma \quad (10)$$

ϵ and χ are the shear and dilatation surface viscosities, μ^* is the bulk viscosity (defined as $\mu^* = \mu_I + \mu_{II}/2$ in two-layer system, as shown in Figure 9), ρ^* is the density (defined as $\rho^* = \rho_I + \rho_{II}/2$), Γ_T is the total adsorption. By way of simplification, a is identified for its variation to:

$$a = C - k^2 D_s; \quad (11)$$

$$b = [k^3(\epsilon + \chi) + 4\mu^* k^2]/k\Gamma_T + \rho^* \quad (12)$$

With these definitions, it is possible to say that there are stable regions and unstable regions in the diagram and that the experimental results will be examined in view of such an analysis, where the coupling between reaction and diffusion intervenes with the hydrodynamics because of the difference of density between layers I and II.

Marginal states share the unstable regions with the stable ones, and they can be in an oscillating or a nonoscillating state, depending on their position in the diagram. Such an approach opens a wide range of possibilities for the behavior of the polymer system, and the analysis will now be performed.

DISCUSSION

NMR studies of the polyamide collodion permit us to show that the photoinitiator is without interaction with the polymer in the nonirradiated material and that the UV irradiation evidently leads to the disappearance of the photoinitiator. It seems that the groups with an aromatic cycle, issued from the photocission of the photoinitiator

ether groups, can be grafted on the macromolecular chains.

NMR spectra show that the solvent is in interaction with the polymer in the photosensitive material by the formation of hydrogen bonds. The number of solvent molecules implicated in hydrogen bonds increases after UV irradiation. The relief formation could be because of the migration of the solvent molecules from the nonirradiated zones to the irradiated zones as a result of the photochemical reactions in the UV-irradiated areas consuming both the initiator and the solvent. A simple photochemical mechanism can be proposed. Photo-cross-linking of the polyamide terpolymer should also be considered.⁸⁻¹⁰

Interesting results with the two-dimensional analysis have been obtained for the samples' reliefs after irradiation under a grating with 20 lines/mm. Figure 5a to 5i gives the representation of the profile for a few samples with an increasing weight loss of solvent. It clearly appears that the profile goes from being quite symmetrical to a double sinusoidal form and, finally, to quite being irregular, with a very low height (on the order of a few hundred nanometers) for the sample with the highest weight loss; thus, various kinds of profiles are observed. For the maximal height corresponding to a weight loss of 82.5%, the relief has a quite regular sinusoidal form and has a height of nearly 1200 nm.

The results seen with the increasing weight loss of solvent, as shown in Figure 5, are the best illustration of the great complexity and sensitivity of this polymer system. The fact that the profiles are at first quite symmetrical and then become double and, finally, are quite inexistent is characteristic of an evolution of the stability of the system. The study of the variation of the $C - k^2 D_s$ entity illuminates the evolution of the system well, and this as seen before, corresponds to the coordinate a evolution on the diagram.

An interpretation can be done using the stability diagram seen in Figure 8. It is possible to consider that in area 1, where the relief has a symmetrical shape, a domain of stability is obtained as a result of the less viscous state of the material because of a higher solvent content. So diffusion is facilitated, and $C - k^2 D_s$ is negative

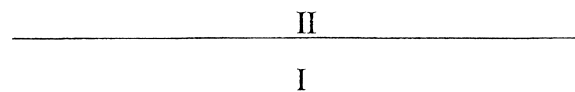


Figure 9 Two layer system.

because of the high diffusion coefficient. Afterward, in area **2**, the system becomes more unstable, with a positive value of $C-k^2D_s$ as a result of a higher photochemical reactivity and a lower diffusion in a more viscous mixture. And in area **3**, the system is too viscous, so the diffusion coefficient is lower, as is the reactivity. The expression $C-k^2D_s$ again can become negative, as C is lower because of the higher viscosity connected to a weaker solvent content. So this approach using the stability diagram with three regions gives a good representation of the evolution of the system as a function of the solvent content for the same amount of irradiation.

In the stability diagram, the evolution is from a less viscous system to a highly viscous system. The abscissa increases from domain **1** to domain **2** and decreases again from domain **2** to domain **3**. Thus, this diagram is a good representation of the system behavior under a grating with 20 lines/mm. Another important point is that the material becomes transparent after irradiation.

CONCLUSION

Considering the interest brought to the polyamide films with the advent of new self-developing properties, it seemed to be of utmost importance to understand the mechanism of their formation. The collodion obtained by the evaporation of the solvent in the polyamide terpolymer-solvent mixture has specific properties, which are directly dependent on the residual solvent content. The relief obtained after UV irradiation can vary drastically depending on the residual content exposed to the same amount of irradiation.

The photopolymer profile can be compared with the general thermodynamic approach proposed in irreversible process thermodynamics for a surface hydrodynamic deformation connected with reaction-diffusion coupling.

An NMR study shows that the photoinitiator is consumed in the irradiated area and leads to grafting on the polymer chains. The solvent is in interaction with the polymer by the formation of hydrogen bonds, especially after the UV irradiation. So it seems that there is migration of solvent molecules. A mechanism of reaction can so be proposed.

All these results give an overview of the peculiar behavior of this new material. From a fundamental point of view, the self-developing properties are connected to the reaction-diffusion coupling during the UV irradiation, leading to a two-

layer system with viscosities that differ between the surface and at the bottom of the field deposited on a glass plate. Work is still in progress for the study of self-developing properties as a function of the length of irradiation or as a function of the grating's spatial frequency. Each kind of profile shape leads to a typical diffraction figure.¹³

This study provides a new insight into this type of material, whose broad properties permit us to consider its use, for example, in the field of information storage.

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