

Barrier Behavior Hindering Zn⁺⁺ Diffusion from Cold Remote Nitrogen Plasma-Deposited Silicon Films

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ABSTRACT: Cold remote nitrogen plasma (CRNP) process is used to deposit organosiloxane polymeric films. 1,1,3,3-tetramethyldisiloxane (TMDS) or its mixture with oxygen is used to deposit polymeric layers on a rubber disks at ambient temperature. The deposited films appear to be efficient against chemical agents diffusion from the disks to a distilled water surrounding phase. The barrier efficiency is increased for films deposited from a TMDS/O₂ mixture. The extracted quantity of Zn⁺⁺ after 30 days of immersion in distilled water at ambient temperature is 70% lower in comparison to the uncoated ones. The transfer of Zn⁺⁺ into a liquid phase for coated disks is also discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 699–705, 1997

Key words: thin films; cold plasma; diffusion; organosiloxane; remote nitrogen plasma; barrier diffusion; plasma deposition

INTRODUCTION

Thin polymeric films have been subject of numerous previous works, due to their many attractive and very interesting mechanical,¹ electrical,² or biocompatibility³ properties. There are a large number of methods to deposit such films. Plasma-enhanced chemical vapor deposition (PECVD) is one of the widely used process for deposition of polymeric films.⁴ Nevertheless, with the PECVD process there is always some substrate damage induced to sensitive substrates by high-energy particle bombardment from the plasma. Among the numerous varieties of plasma-assisted polymerization techniques, Remote PECVD (RPECVD) has recently attracted considerable interest to tackle this disadvantage.⁵ In the RPECVD process the substrate is removed from the plasma as the plasma and the reaction chamber are spatially separated.^{6–8} Plasma-deposited organosiloxanes films have many attractive properties; numerous studies have been devoted to the permeability of plasma

polymers with the aim of increasing selectivity for membrane separation processes.^{9,10} In several applications, such as foodstuffs, cosmetics, and packaging, polymer or rubber materials are in contact with some liquid surrounding the medium, in this case, chemical agents can migrate from the material into the liquid. When some pharmaceutical rubber cups are in contact with distilled water, the liquid penetrates into the material, and such chemical agents such as Zn⁺⁺ migrate into the distilled water (or into a pharmaceutical liquid phase) with the following results: 1) the surrounding medium is contaminated by the chemical additives; 2) the material shows a deterioration of mechanical properties.

We have developed a plasma deposition process induced by cold remote nitrogen plasma (CRNP). Specific industrial aspects of this plasma have been protected by international patents.^{11,12} The main reactive species of CRNP are nitrogen atoms, free radicals, and electronically and vibrationally excited nitrogen molecules. The CRNP is then a nonionized reactive zone and is characterized by an important thermodynamic nonequilibrium state¹³: the translation temperature is

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roughly the ambient temperature but the vibrational temperature Tv depends on the pressure range (for $P = 1000$ Pa, $Tv = 2500\text{--}3000$ K).

The present work deals with the study of the barrier effect hindering Zn^{++} diffusion from rubber with CRNP-deposited thin polymeric films of tetramethyldisiloxane (TMDS). The barrier behavior is also discussed as a function of oxygen admixture to TMDS. Transfer kinetics and the effects of such parameters as temperature and initial ZnO concentration in the material are investigated to evaluate the barrier efficiency of the deposited films.

THEORETICAL

When rubber disks are immersed in distilled water, the Zn^{++} ions diffuse from the solid to the liquid. Zn^{++} is transferred from the solid into the liquid phase by three steps process: (1) Zn^{++} transport in the rubber, (2) Zn^{++} transport at the solid-liquid interface, and (3) Zn^{++} transport into the solution.

The two phases are regarded as balanced at their interface for Zn^{++} concentration, and we assume the transfer resistance through that interface to be negligible.

The following assumptions are made to study transfer into liquid phase: (1) diffusion is one dimensional in an isotropic medium bounded by two parallel planes at $x = \pm L$, where $2L$ is the thickness of the disk; (2) the diffusion is a nonsteady state phenomenon; and (3) at time $t = 0$ of the disks immersion into a liquid, the concentration of Zn^{++} is constant in the solid and equals to zero on its faces.

The diffusion is defined by Fick's law and can be written in these conditions as:

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x} \left(D \frac{\delta C}{\delta x} \right) \quad (1)$$

where the diffusion coefficient (D) depends on the concentration (C) of diffusing Zn^{++} , t is the time and x is the abscissa measured through the thickness of the disk.

The boundary conditions are:

$$\begin{aligned} t = 0 \quad -L < x < +L \quad C &= C_0 \\ x = \pm L \quad C &= 0 \\ t > 0 \quad -L < x < +L \quad C &= f(x, t) \\ x = \pm L \quad C &= 0 \end{aligned}$$

Table I Rubber Disks Composition

$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}=\text{C}-\text{CH}-\text{CH}_2- \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$
98%	1.5%	
Copolymer structure		
Stabilizing agent	Calcium stearate	
Antioxidant	Phenolic	
Mineral charge	Calcinated Kaolin: Al_2O_3 ; SiO_2	
Vulcanization agent	ZnO	
Pigment	Iron oxide	

If M_t denotes the total amount of diffusing substance that left the solid at time t and M_∞ the corresponding quantity after infinite time, the Zn^{++} transfer into the liquid is given by the very well-known equation where D is assumed to be constant:

$$\frac{M_\infty - M_t}{M_\infty} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left(-D(2n+1)^2 \frac{\pi^2}{4L^2} t\right) \quad (2)$$

Equation (2) converges rapidly and only the first term is significant for long diffusion times. It can be then written as:

$$\text{Log}\left(\frac{M_\infty - M_t}{M_\infty}\right) = \text{Log}\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2 t}{4L^2} \quad (3)$$

In order to evaluate the barrier efficiency of the deposited films, diffusion coefficient for uncoated films will be determined from eq. (3).

EXPERIMENTAL

Material

Disks (2 mm thick) having diameter 25 mm were prepared from an elastomer Isoprene (98%) chlorinated Isobutylene (1.5%) copolymer and are provided by Stelmi S. A. France. The stabilizing and additive agents represent 0.5%. The composition of the material is given in Table I.

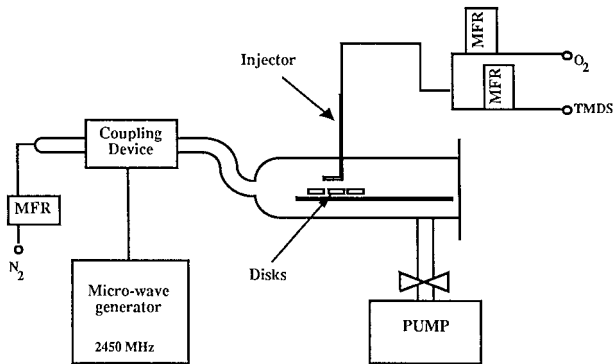


Figure 1 Schematic diagram of the experimental setup.

Plasma Device

Figure 1 shows the experimental setup of a CRNP-assisted deposition reactor. Nitrogen is introduced, under a pressure of 5 hPa at a flow rate of 1.8 slpm in a Pyrex discharge tube of 33 mm outer diameter. The discharge excitation is created by a Moreau-type rectangular coupling device at 2450 MHz.¹⁴ The gas containing excited species is extracted from the discharge zone by a primary pump, ALCATEL 33 m³/h. The monomer is 1.1.3.3-tetramethyldisiloxane (TMDS) (97% purity) purchased from Aldrich Chemical Co. It is vaporized under experimental conditions. Its flow rate, kept constant, is equal to 80 sccm. The reactive gas (TMDS) is injected in the reaction chamber through a coaxial injector at a distance of 1.5 m downstream from the discharge. Such a distance avoids substrate damage induced by the charged particles.

Fifteen disks are disposed horizontally in the reactor on a surface of about 8 × 13 cm² and are coated on each face. The samples are totally coated in two steps; these two steps are separated by an open air operation. To obtain homogeneous deposits, the distance between the substrates holder and the coaxial injector axis is kept constant at 8 cm. Under these conditions, the dispersion in term of film thickness is less than 5% for a coated surface of 10 × 15 cm².

Nitrogen is Air liquide 'U' grade and oxygen is Air liquide 'C' grade. The reactor pressure is controlled by an Edwards PRH 10 Pirani type vacuum gauge. The flow rates of gases are regulated by Alphagaz RDM 280 mass flow regulators (MFR).

The incident microwave power is maintained constant and equal to 200 W. The oxygen is mixed to the constant TMDS flow rate. The deposition time is taken equal to 5 min for each face. The

studied films denoted TMDS1, TMDS2, TMDS3, and TMDS4 correspond, respectively, to oxygen flow rates of 0, 5, 10, and 15 sccm.

Diffusion Measurements

Five disks were immersed in distilled water in a closed Pyrex vessel. The extractions were realized under isothermal conditions in a stationary liquid without any stirring effect at three different temperatures. The Zn⁺⁺ concentration in the liquid was evaluated by atomic absorption with a VARIAN AA6 spectrometer.

RESULTS

Uncoated Material

Effect of the Concentration

Experiments are carried out at different temperatures by working with rubber disks containing two different ZnO (which is the initial form of Zn⁺⁺ in the solid) concentrations 2.5 and 5% weight in ZnO. The percentages are relative to 100 g of stabilizing and additive agents. The values of Zn⁺⁺ concentration in distilled water (ppm) vs. time of immersion (days) at ambient temperature are shown in Table II. It clearly gives evidence that the extraction slightly varies with the initial ZnO concentration in the material. The kinetic of Zn⁺⁺ diffusion appears more rapid for the material containing the lower ZnO concentration, which is in disagreement with the Fick's diffusion law. This result is explained by the fact that ZnO is a vulcanizing agent, so the higher concentration of ZnO is, the more crosslinked is the material and the Zn⁺⁺ extraction difficult, then the diffusion kinetic is slower.

Effect of the Temperature

Tables II, III, and IV show results on diffusion kinetics at different temperatures: ambient, 40 and 60°C for two initials concentrations of ZnO in the material. The extraction data show the importance of the temperature effect on the migration rate, the kinetic of the Zn⁺⁺ migration is accelerated by increasing the liquid temperature.

The concentration after 30 days of immersion in distilled water $M_{30 \text{ days}}$ is different for the three tested temperatures (Table III). For experiments at ambient and 40°C, the equilibrium seems not to be achieved. However, for the experience at

Table II Evolution of the Zn⁺⁺ Extracted Quantity in Distilled Water vs. Time of Immersion

Time of Immersion (Days)	Disks with 2.5% in ZnO (ppm)			Disks with 5% in ZnO (ppm)		
	Ambient	40°C	60°C	Ambient	40°C	60°C
4	0.498	0.682	0.981	0.446	0.670	0.814
8	0.689	0.966	1.597	0.623	0.907	1.300
15	0.911	1.703	2.743	0.879	1.384	2.178
21	1.208	2.538	3.005	1.178	1.997	2.892
30	1.371	2.786	3.114	1.343	2.294	3.037

60°C, the extracted quantity of Zn⁺⁺ reaches a plateau value of 3.114 ppm after 21 days of immersion in the liquid phase, which gives evidence that an equilibrium state is achieved.

For diffusion coefficient calculations, we make the hypothesis that M_{∞} value is the same for the three temperatures and equal to the concentration extracted after 30 days of immersion at 60°C:

$$M_{\infty} \text{ at ambient temperature} = M_{\infty} \text{ at } 40^{\circ}\text{C} \\ = M_{\infty} \text{ at } 60^{\circ}\text{C} = M_{30 \text{ days}} = 3.114 \text{ ppm.}$$

Figure 2 shows that Zn⁺⁺ concentration in distilled water obeys to a kinetic law according to eq. (3). Diffusion coefficients calculated by using this equation and the corresponding correlation coefficients are presented in Table IV. The correlation coefficients are close to 1. The hypothesis made for diffusion coefficients calculation is then good. The calculated ratio between the diffusion coefficient at 60°C and the diffusion coefficient at ambient temperature is about nine ($D_{60^{\circ}\text{C}}/D_{\text{ambient}} \approx 9$). This result means that extraction rate is very low at ambient temperature and is closely dependent on the liquid phase temperature. This agrees with the observation that the equilibrium is not achieved after 30 days of immersion in the liquid phase at ambient temperature.

Table III Evolution with the Liquid Phase Temperature of the Zn⁺⁺ Extracted Quantity for Disks Containing 2.5% in ZnO after 30 Days in Distilled Water

Temperature (°C)	Extracted Quantity (ppm)
Ambient	1.371
40	2.786
60	3.114

Coated Material

Effect of Dioxygen Addition

Figure 3 shows the extraction profiles for coated disks at ambient temperature for a material containing 2.5% weight in ZnO. It shows that the barrier efficiency is enhanced when oxygen is added to the TMDS monomer. The higher is the oxygen flow, the lower is the extracted Zn⁺⁺ concentration. It is very well known that oxygen addition to monomers increases deposition rate,¹⁵ so the films deposited without any oxygen addition (TMDS1) are thinner and the Zn⁺⁺ extraction is then easier.

For films deposited with TMDS/O₂, the increase of the barrier efficiency can be explain by the fact that the films are more crosslinked.^{7,15} Callebert et al.⁷ proved that silica-like structure films are deposited from the reaction between CRNP and TMDS and that highly hydrocarbonated crosslinked polysiloxane network is obtained with the TMDS/O₂ mixtures.

The extracted Zn⁺⁺ quantity after 30 days of immersion is 0.403 ppm for disks coated with TMDS4 and 1.317 ppm for uncoated disks. Then it decreases by about 70%, which gives evidence of the high performance of the deposited films as a barrier against Zn⁺⁺ diffusion.

Figure 3 also shows that extraction profiles for coated disks are different from those obtained with the uncoated ones. The extracted Zn⁺⁺ concentration increases slowly for coated disks in comparison to the uncoated ones; the diffusion kinetic is then blocked by the deposited films and particularly for short immersion times. The migration phenomenon seems to be governed by diffusion through the deposited film for short immersion times (less than 15 days). For long times, the concentration through the deposited films becomes homogenous, Zn⁺⁺ is dispersed all over the

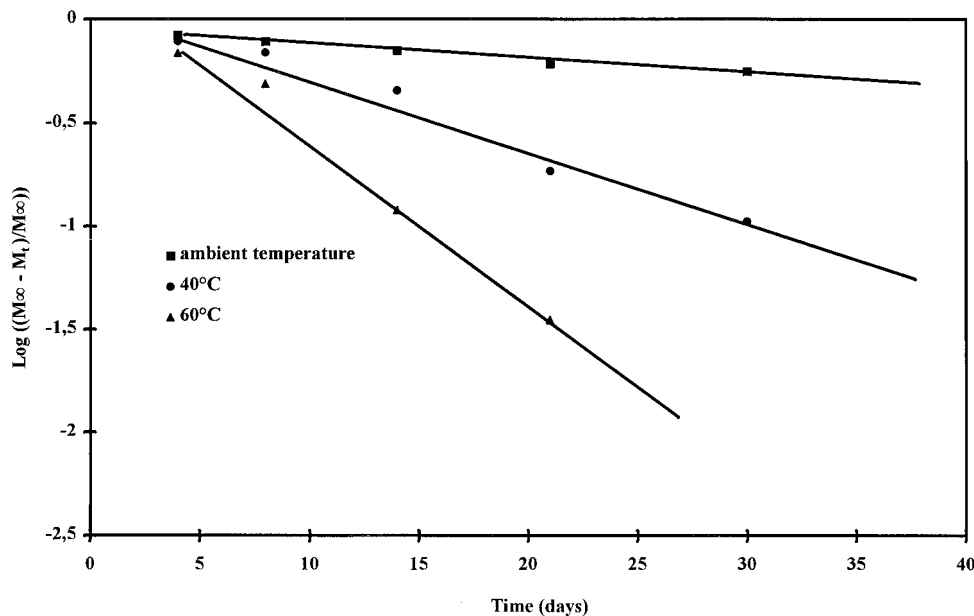


Figure 2 Diffusion coefficients calculation according to eq. (3) for the material containing 2.5% weight in ZnO.

deposited films, and only then is the migration controlled by the diffusion through the disk.

The barrier formed by the deposited films hindering Zn^{++} diffusion can be related to the very low superficial energy due to a specific surface structure of the deposits. Water drop contact angle measurements show high values ($>160^\circ$) on the deposited films.⁷ This low superficial energy is explained by a preferential orientation of apolar methyl groups outside the interface. This particular surface aspect leads to a more difficult distilled water penetration through the disk, and then the Zn^{++} diffusion from the disk to liquid phase is inhibited.

Effect of the Temperature

Figure 4 shows the effect of the temperature of the liquid phase on the Zn^{++} diffusion kinetic for disks coated with TMDS4. As we have demonstrated for uncoated disks, the migration rate is accelerated by increasing the temperature. For coated disks, the barrier efficiency is preserved for extraction at ambient temperature and at 40°C. However, at 60°C the barrier efficiency decreases significantly after 21 days. This can be due to a degradation of the deposited films for long immersion times leading to a complete disappearance of the barrier effect.

CONCLUSION

The barrier efficiency to Zn^{++} diffusion of films deposited from 1,1,3,3-tetramethyldisiloxane (TMDS) is demonstrated. It is increased for those deposited from TMDS/O₂ mixtures. The extracted quantity of Zn^{++} after 30 days of immersion in distilled water at ambient temperature is divided by nine in comparison with the uncoated ones. The transfer of Zn^{++} into a liquid phase for coated disks is shown to occur in two distinct periods. In the first period, for any time lower than 15 days, the Zn^{++} concentration in the liquid increases linearly; the diffusion is then controlled by diffusion through the deposited film. In the second period, for time higher than 15 days, Zn^{++} transfer is governed by internal diffusion through the disk.

Table IV Calculated Diffusion Coefficients in Distilled Water for Disks Containing 2.5% in ZnO and the Corresponding Correlation Coefficients for Different Temperatures

Temperature (°C)	Diffusion Coefficients (cm ² /s)	Correlation Coefficients
Ambient	$0.71 \cdot 10^{-9}$	0.99
40	$3.38 \cdot 10^{-9}$	0.98
60	$6.01 \cdot 10^{-9}$	0.99

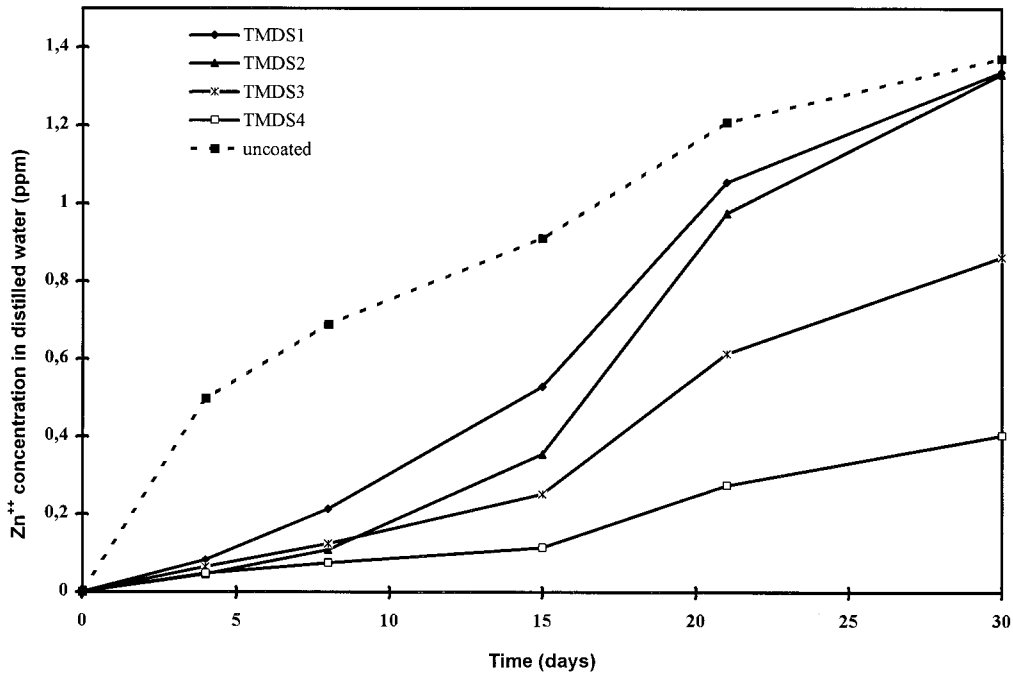


Figure 3 Evolution of the extraction profiles for coated disks containing 2.5% weight in ZnO at ambient temperature with dioxygen flow rate (ΦO_2); TMDS1: $\Phi O_2 = 0$ sccm; TMDS2: $\Phi O_2 = 5$ sccm; TMDS3: $\Phi O_2 = 10$ sccm; TMDS4: $\Phi O_2 = 15$ sccm.

The present process is now applied to coat industrial sanitary rubber articles for medicaments packaging in order to improve their surface prop-

erties and to avoid chemical agents diffusion. Results on the performance of a such industrial process will be published in a future article.

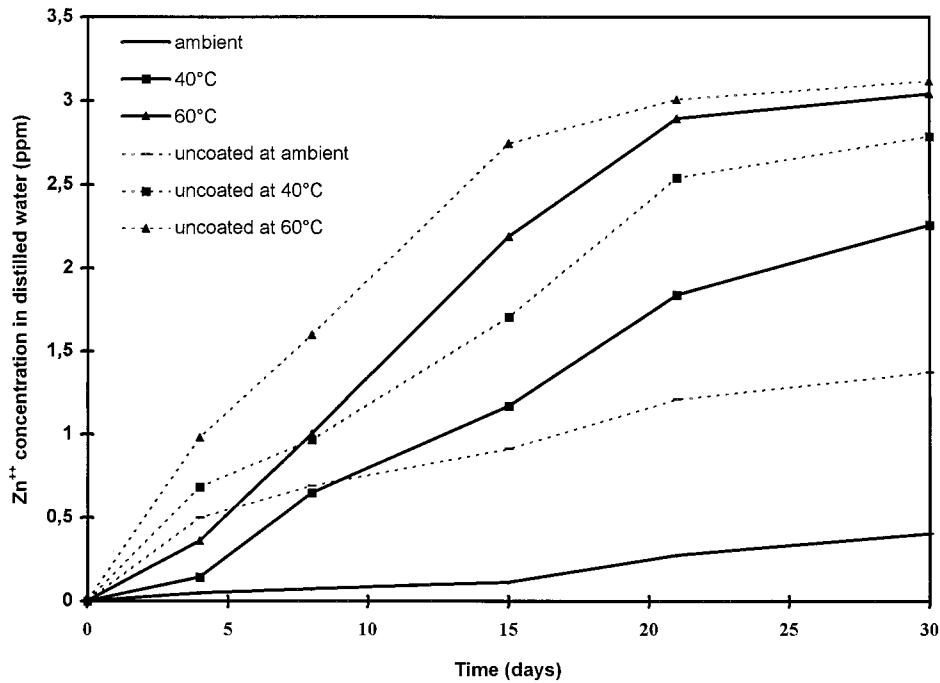


Figure 4 Effect of the temperature of the liquid phase on Zn⁺⁺ diffusion kinetic for disks coated with TMDS4.

REFERENCES

1. D. L. Cho and H. Yasuda, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **42**, 73 (1988).
2. H. Yasuda, *Plasma Polymerization*, Academic Press, Orlando, FL, 1985.
3. D. Kiaei, A. S. Hoffman, D. B. Ratner, T. A. Horbett, and L. O. Reynolds, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **42**, 269 (1988).
4. H. V. Boenig, *Fundamentals in Plasma Chemistry and Technology*, Technomic, Lancaster, 1988.
5. J. L. Vossen and W. Kern, *Thin Films Processes II*, Academic Press, San Diego, 1991.
6. C. Jama, Thesis No. 1554, Lille, France (1995).
7. F. Callebert, Ph. Supiot, K. Asfardjani, O. Dessaux, P. Goudmand, P. Dhamelincourt, and J. Laureyns, *J. Appl. Polym. Sci.*, **52**, 1596 (1994).
8. B. Mutel, A. Ben Taleb, O. Dessaux, P. Goudmand, L. Gengembre, and J. Grimblot, *Thin Solid Films*, **266**, 119 (1995).
9. J. Sakata, M. Hirai, and M. Yamamoto, *J. Appl. Polym. Sci.*, **34**, 2701 (1987).
10. N. Inagaki, S. Kondo, M. Hirata, and H. Urushibata, *J. Appl. Polym. Sci.*, **30**, 3385 (1985).
11. K. Asfadjani, C. Jama, O. Dessaux, P. Goudmand, and L. Caburet, FR 95/05333 (1995).
12. F. Callebert, C. Dupret, O. Dessaux, and P. Goudmand, Intern. Pat. Application, WO 92/03591 (1992).
13. B. Mutel, M. Bridoux, M. Crunnelle-Cras, O. Dessaux, F. Grase, P. Goudmand, and G. Moreau, *Chem. Phys. Lett.*, **2**(3), 290 (1984).
14. G. Moreau, O. Dessaux, and P. Goudmand, *J. Phys. E: Sci. Instrum.*, **16**, 1160 (1983).
15. C. Jama, J. D. Quensierre, O. Dessaux, and P. Goudmand, 11th ISPC, Loughborough, 1047 (1993).