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Submicrometre ablation on polymer surfaces

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Abstract

Since 1992, we have demonstrated that a UV laser beam of uniform profile and low energy in well-defined conditions can give rise to spontaneous submicrometre periodic structures. In this work, new results are presented for two polystyrene systems using KrF excimer laser radiation. The new irradiation set-up is described, which includes diagnostics based on the diffraction of an HeNe beam by the periodic structures in order to record their growth. The kinetics of structuring are recorded for several laser intensities. In the optimum experimental conditions, poly(α-methylstyrene) samples show a double periodicity in two perpendicular directions. Microscopic observations reveal that the new surface is composed of 0.25 μm beads dispersed in a regular matrix having a submicrometre period. These small beads are easily detached from the surface by a mechanical force (rubbing). The mechanisms of formation are discussed in terms of the excitation of surface waves and the formation of submicrometre droplets during irradiation. © 1997 Elsevier Science S.A.

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1. Introduction

Several reports have demonstrated that laser ablation achieved with a beam of UV radiation is a high-resolution etching process even for heat-sensitive materials such as polymers [1]. Submicrometre structuring can be obtained with patterned beams as in microlithography or by two-beam interference. Two-beam interference was reported by Ilcisin and Fedosejevs [2] in 1987 for the direct production of gratings on plastic substrates using KrF laser radiation. Gratings with a period of 0.5 μm were made on poly(ethylene terephthalate) films, as well as on other polymers, showing that submicrometre resolution can be readily achieved if UV laser radiation is used. A similar experimental approach has been used more recently by Phillips et al. [3] for the direct ablation of sub-100 nm line structures into polyimide. In other experiments, Spiess and Strack [4] have used a contact mask in order to pattern finely the excimer laser beam. Contact masks are used in microelectronics and are made of a patterned chromium layer deposited on a silica or quartz window. The advantage of placing the mask in contact with the sample to be etched is that there is less limitation due to diffraction of the beam than when the mask projection technique is used. The contact mask method is a simple approach since no precise alignment is necessary and submicrometre ablation of polyimide layers has been demonstrated. However, complications were identified due to the deposition of ablation products on the mask surface. This is clearly a serious drawback to eventual applications. Therefore the mask projection technique can be used advantageously as demonstrated by Goodall et al. [5] in 1990. For high-resolution beam patterning, it requires a large numerical aperture projection lens which meets the necessary broad-band spatial frequency transmission. Similar optics are used industrially in microlithography, but at a much lower intensity (a few mJ cm^{-2}) than in the case of direct ablation (1–10^4 mJ cm^{-2}). In principle, ablation with this technique using ArF radiation can reach the same limit as for microlithography (approximately 0.15 μm).

In addition to these conventional techniques, we have demonstrated since 1992 [6–12] that homogeneous UV beams of excimer lasers can pattern finely polymer surfaces at the submicrometre level to yield so-called photochemical submicrometre periodic structures. In these experiments, the beam is linearly polarized, its profile is uniform and its energy is set at a subthreshold value, so that ablation is kept at a very low level. Structuring is made possible by the excitation of a surface wave (SW), whose interaction with the incident beam provides a modulation of intensity only on the surface. This technique has been applied successfully to a variety of

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polymers, including polyesters, thermostable polymers such as polyimides and polystyrenes. So far, we have reported results on highly absorbing polymer surfaces with either ArF or KrF radiation. The techniques of characterization used were scanning electron microscopy and ellipsometry which are well adapted to the study of periodic structures with extremely small periods (150–250 nm). In the new systems, presented in this work, larger structures are created with periods ranging from 250 to 800 nm. The advantage of using these systems stems from the fact that they can diffract visible light. Therefore they can easily be seen by the experimenter, and an HeNe laser beam can be used to record the growth of structure as indicated below. The polymers studied were polystyrene (PS) and poly(α-methylstyrene) (PαMS) irradiated with KrF radiation. It has been shown that hydrocarbon polymers, such as PS, do not structure in the absence of oxygen; therefore irradiation was performed in the presence of air. It is shown that the reaction of oxygen with the surface to yield new functionalities with high sensitivity to ablation is essential for submicrometre periodic structuring. In this study, the influence of experimental conditions, such as the laser energy, is described, and evidence for an optimum energy density is given. The kinetics of structuring are also determined precisely using in situ monitoring of the diffracted light. The various stages of structuring reveal that PαMS gives a droplet matrix rather than a simple line structure as in the case of PS. This behaviour is unique and provides a new surface with original properties.

Excimer laser submicrometre structuring is an appealing technique for the generation of surfaces with original properties on a large scale. Since no precise alignment between the beam and surface is needed, scanning the surface with laser radiation is possible and allows a large surface area to be covered. Of the properties which can be improved by this technique, the following can be cited: friction, wettability, liquid crystal alignment, epitaxy, adhesion, adsorption, particle trapping, optical properties, aerodynamics, hydrodynamics, etc. The structured polymer can also be used as a resist for the dry etching of hard substrates such as silicon. This has been demonstrated recently by Hiraoka and Wong [13]. In contrast with earlier work [14], in which structuring occurred during ablation with high-energy pulses, this new method keeps ablation at a minimum and gives, in a controlled manner, a periodicity exclusively in the submicrometre range.

2. Experimental details

2.1. Irradiation procedure

The polymer samples were irradiated essentially as described previously [7]. However, by experimenting with PαMS at 248 nm, new diagnostics were introduced based on the diffraction of an HeNe beam as displayed in Fig. 1. The surface is irradiated at incidence θ with a KrF beam of 5 mm

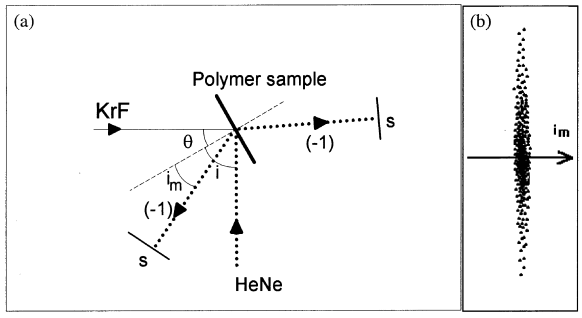

Fig. 1. (a) Experimental set-up, including the new HeNe beam diffraction method introduced to monitor structural growth. KrF beam polarization is perpendicular to the plane of incidence. The sample is irradiated in the TE configuration. S are screens or photodiode detector. (b) Diffraction spot (order -1) observed on the screen S in reflection or transmission.

in diameter and analysed with an HeNe beam (1 mm in diameter) placed at incidence i, so that the -1 diffraction order is at i_m with $m = -1$. These angles are related to each other by the grating formula

$$m\lambda_{\mathrm{HeNe}} = \Lambda(\sin i - \sin i_m) \quad (1)$$

where λ_{HeNe} is the HeNe laser wavelength and Λ is the period of the structure. With periods of the order of 500 nm used in this work, only one order (-1) of diffraction is usually observed. It should be noted that this order can equally be observed in reflection or transmission when a transparent substrate is used. A typical diffraction spot is displayed in Fig. 1(b) and can be observed when a screen is placed at position S in Fig. 1(a). It is fairly narrow in the horizontal plane, but fairly stretched in the vertical direction (parallel to the submicrometre periodic structure lines) due to structural irregularities inducing HeNe laser light diffusion. The intensity of the HeNe line at 632.8 nm was measured with a silicon photodiode (Photonetics) in the diffraction spot, most commonly placed in the plane of incidence, i.e. along the i_m axis in Fig. 1(b). The diffracted light intensity $I(i_m)$ recorded in this plane reflects the distribution function of the period of the structure in the samples.

All irradiations were performed in air since the presence of oxygen is necessary to obtain structuring.

2.2. Sample preparation

Most of the polymer films were coated on microscope glass, either by spin coating or dip coating from a polymer solution in toluene. The two polymers used were PαMS and PS which were purified by successive precipitation of toluene solutions in methanol. It was observed that PαMS structures more strongly than PS in the same conditions.

2.3. Characterization of submicrometre periodic structures

Of the microscopic techniques, scanning electron microscopy (SEM) is the most effective, giving sharper details of the surface. With atomic force microscopy, it is difficult to observe the modified polymer surfaces owing to the tendency

of the polymer to stick permanently to the probe tip. In some instances, optical microscopy can be used, especially for in situ observation and irradiation.

3. Results and discussion

3.1. Excitation of surface waves

A simple theory assumes that a surface wave is excited by the incident beam. Let us discuss how such waves can be generated. In Fig. 2, a scattering centre (SC) is considered to be the source of a scattered spherical wave which is decomposed in this calculation into two waves $2\pm$ propagating in opposite directions in the plane of incidence

$$\text{Wave 1: } E_1 = E_{10} e^{i(\omega t - k_1 \sin \theta x)} \quad (2)$$

$$\text{Wave } 2\pm: E_2 = E_{20} e^{i(\omega t \pm k_2 x)} \times e^{-\alpha x} \quad (3)$$

$$I \propto (E_1 + E_2)(E_1^* + E_2^*) \quad (4)$$

$$I \propto E_{10}^2 + E_{20}^2 + 2E_{10}E_{20} \cos(k_1 \sin \theta \pm k_2)x \quad (5)$$

Wave vectors are denoted as k, θ is the angle of incidence of wave 1 and α is the absorption coefficient for the attenuation of wave 2 at the surface along the direction of propagation x. I is the radiation intensity at the surface.

The modulation period Λ is the value of x which verifies

$$(k_2 \pm k_1 \sin \theta)\Lambda = 2\Pi \quad (6)$$

Therefore

$$\Lambda \pm = \frac{\lambda_0}{n \pm \sin \theta} \quad (7)$$

in which λ_0 is the laser wavelength and n is the refractive index of the medium in which wave 2 propagates. This simple theoretical approach accounts well for the experiments, as shown in Fig. 3 for PαMS, except that only $\Lambda-$ is usually observed. Scattering centres randomly dispersed on a surface (Fig. 2(b)) produce wavelets which interfere destructively,

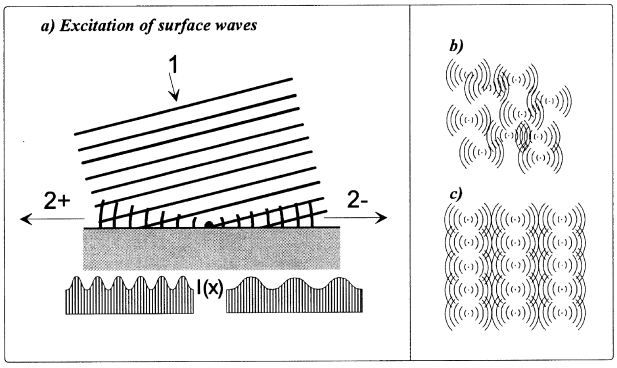

Fig. 2. (a) Excitation of a new wave 2 by a scattering centre (SC) of the surface results in a modulation of intensity $I(x)$ by interference with the main wave 1 (laser beam). (b) SCs placed randomly interfere negatively. (c) SCs placed on a grating of period Λ interfere constructively; this is the resonance position.

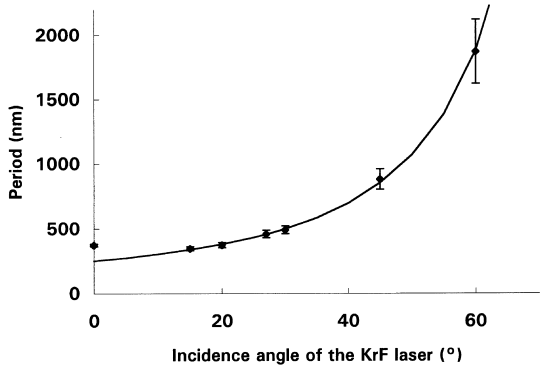

Fig. 3. Variation of the structural period with the angle of incidence θ of the KrF laser, measured by the HeNe light diffraction method. The full line is obtained with Eq. (7) adjusted to the best fit with $n = 1$.

whereas if they are placed periodically with Λ spacing as in Fig. 2(c) (the Wood anomaly condition [15]), they interfere constructively. This explains why grating-like structures appear on the surface, since the original surface roughness, in its spectrum of Fourier spatial frequencies, contains such a grating, meeting the resonant condition. At the beginning of irradiation, the surface wave amplitude is low, but increases as the ablation proceeds. Such surface waves can be named polarization waves for dielectrics, since they can be due to oscillating polarization surface charge [16]. Similar phenomena are due to surface plasma waves in the case of free electron materials, such as metals or semiconductors. A review of the past literature is given in Ref. [7] and reveals that the periodic structuring of polymers is an entirely new field, whose interest is growing rapidly.

3.2. Kinetics of structuring

The development rate of structuring can be conveniently monitored by in situ measurement of the intensity of HeNe laser diffracted light [17]. A typical diffraction spot is displayed in Fig. 1(b), and the intensity vs. time evolution is assumed to vary in a similar manner to the structural amplitude. For the measurements, the photodiode is moved in the plane of incidence (as a function of i_m) or placed at the maximum diffraction intensity. In previous work, we found that structuring occurs in a well-defined window of fluence always located below the threshold of ablation. For PS and PαMS, the ablation threshold fluence is about 60 mJ cm^{-2}. Fluences above the window tend to melt and erase the structures, whereas below the window the structuring rate is too low. It was observed that the fluence window depends strongly on the polymer structure. From the present results, we can conclude that there is an optimum fluence in the structuring window: 7.2 mJ cm^{-2} of the optimum radiation for PαMS. At this optimum condition, which is called the ''stable condition'', the structures grow faster and larger without any changes in the main spatial period. This is illustrated by the curves in Fig. 4, which represent the diffraction peaks or period distribution function as a function of the KrF laser dose. The main phases of growth are identified as in

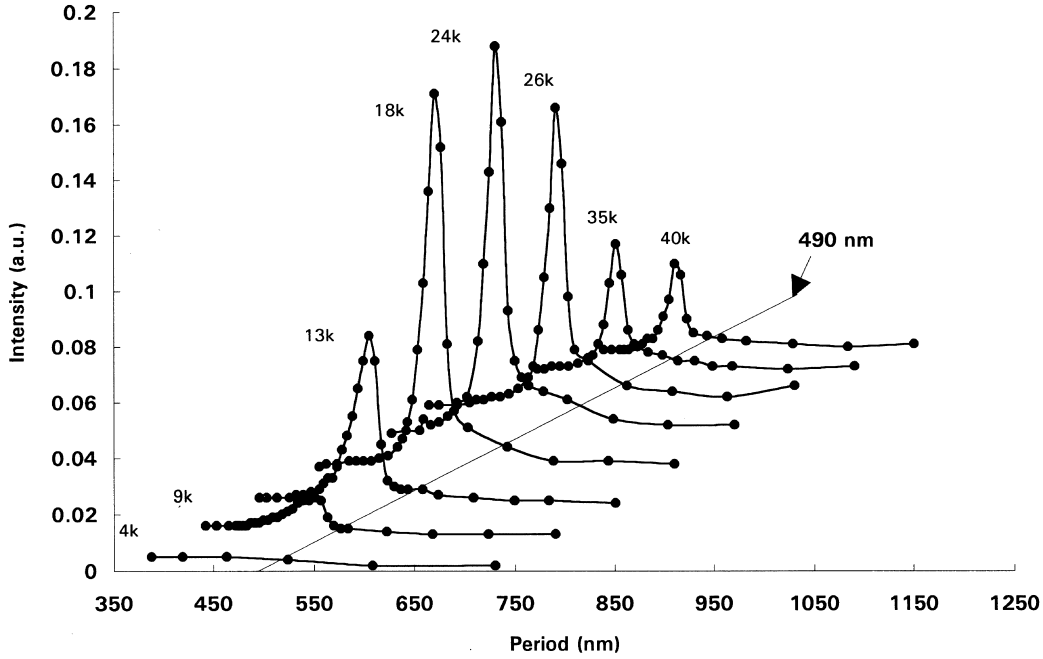

Fig. 4. Kinetics of structuring of the PαMS surface in the so-called stable condition of irradiation (fluence, 7.2 mJ cm^{-2} of KrF; $\theta = 30°$). The intensity of the HeNe beam diffraction spot is recorded as a function of i_m (period given by Eq. (1)) for several values of the total dose given in number of pulses (1K = 10^3 pulses).

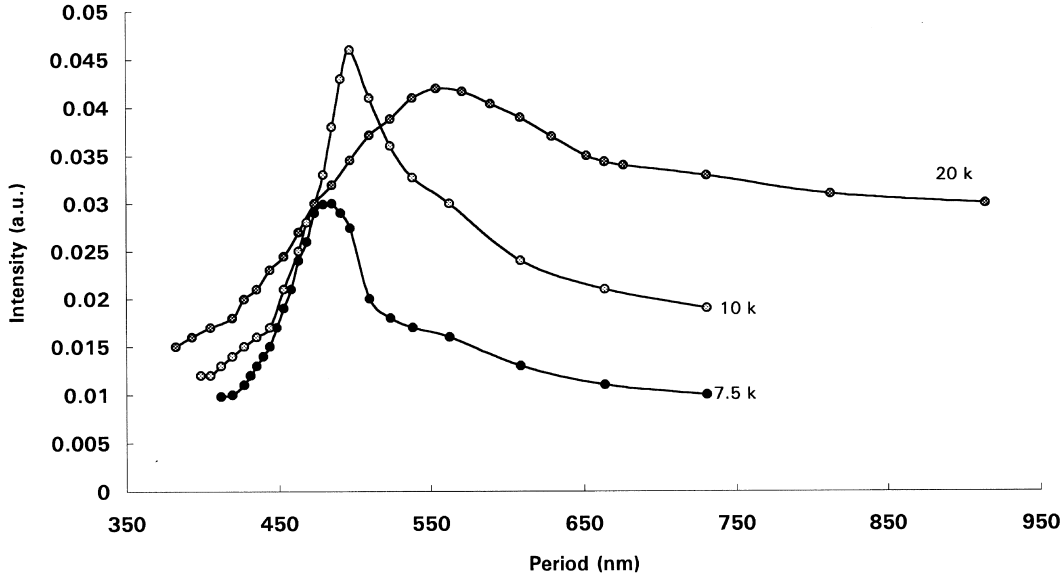

Fig. 5. Kinetics of structuring of the PαMS surface in the so-called unstable condition of irradiation (fluence, 8.5 mJ cm^{-2} of KrF, $\theta = 30°$). The intensity of the HeNe beam diffraction spot is recorded as a function of i_m (period given by Eq. (1)) for several values of the total dose given in number of pulses (1K = 10^3 pulses).

previous work as incubation, growth and decline. It is interesting to note that, even during the decline, the period distribution function remains constant. This is a characteristic of structuring in stable conditions. Unstable conditions, which correspond to a slightly larger fluence (8.5 mJ cm^{-2}), give rise to a drastic change in the period distribution function during irradiation. This case is displayed in Fig. 5 and shows that, even though growth is faster, the structural period function broadens very rapidly to larger periods. For a fluence lower than 7.2 mJ cm^{-2}, structuring is very slow, making the irradiation time too long and not necessarily leading to higher structures.

3.3. Structuring mechanisms

The surface photochemical reaction leading to matter consumption or displacement is essential to structuring. For instance, PS cannot be structured in vacuum since oxygen is needed to develop periodic structures. X-Ray photoelectron spectroscopy (XPS) and Fourier transform IR (FTIR) anal-

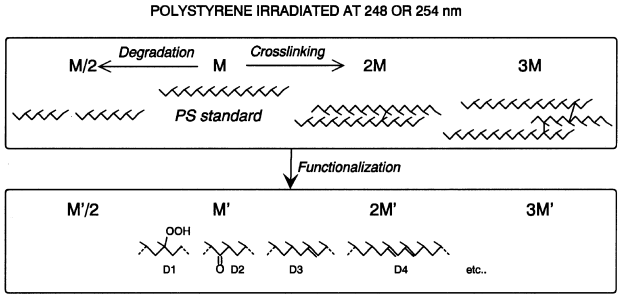

Fig. 6. Various photochemical reactions of the PS or PαMS surface on irradiation with KrF radiation in the presence of oxygen. M is the starting molecular weight distribution. $M/2$, $2M$ and $3M$ are the molecular weight $\times$ (1/2, 2, 3) distributions formed by irradiation. Similarly, M', $M'/2$, $2M'$ and $3M'$ are the distributions of the functionalized polymer molecules formed by irradiation.

ysis have confirmed that the PS surface incorporates oxygen during structuring [18]. Various photochemical reactions involving oxygen molecules are summarized in Fig. 6. Cross-linking reactions have been identified by gas permeation chromatography and functionalization in olefins or oxygen derivatives detected with FTIR. Extensive oxidation may lead to the formation of gas molecules, such as CO_2, resulting in slow photo-oxidative etching of the surface. Therefore the polymer properties are drastically altered by irradiation, in particular the absorption coefficient and thermal properties such as T_g. The modified surface is more sensitive to ablation and also less compatible with the original polymer.

3.4. Formation of new submicrometre droplets on PαMS

As shown in Fig. 7, the PαMS surface displays a unique property after irradiation. It is composed of small beads, 0.25 μm in diameter, periodically dispersed on the surface. The alignment along the horizontal direction is quite remarkable. This corresponds to the previously known line structures, which develop along the polarization direction, with a periodic line spacing matching Eq. (7). Within each line, the

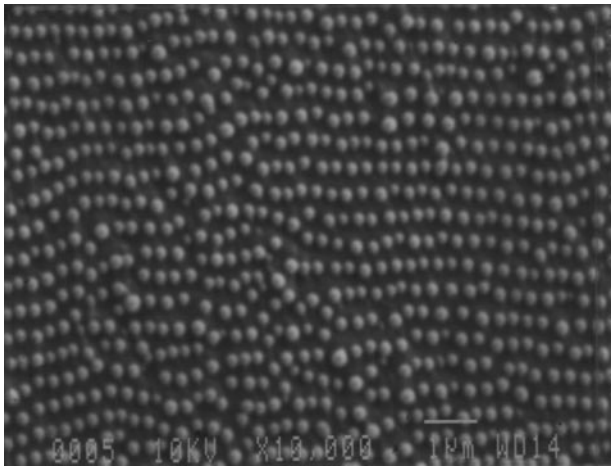

Fig. 7. New submicrometre-sized droplet matrix formation on the PαMS surface irradiated with polarized KrF radiation in the stable condition (7.2 mJ cm^{-2}, $\theta = 30°$, configuration TE).

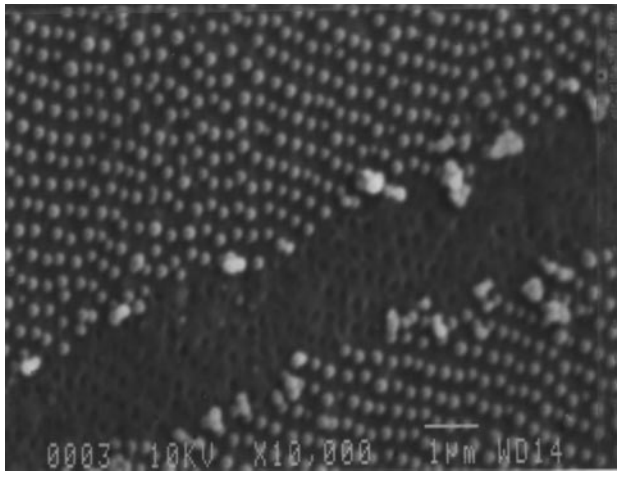

Fig. 8. Droplets of oxidized polymer, obtained by laser structuring, can be detached from the original PαMS substrate by a mechanical force (scratching with paper fibre).

bead spacing is of the order of 0.3 μm and is independent of the angle of incidence. It is suggested that bead formation within a line does not follow a coherent mechanism as in line periodic structures, but rather a thermally driven mechanism. The tendency to form dot patterns spontaneously has been observed in previous work, e.g. on the polycarbonate surface [11] and polyimide [19], but this was observed after extensive irradiation of the line patterns. For PαMS, bead patterns appear even at the beginning of structuring, as observed by in situ optical microscopic observations [20]. Fig. 8 further demonstrates that the beads can easily be detached from the irradiated sample surface. The sample was rubbed very gently with paper before SEM observation; the interaction of a single paper fibre with the bead pattern could be observed; the beads were swept away and collected in a remote position. In addition, it seems that the new bead-free positions are marked by submicrometre holes. From this experiment, we can conclude first that there is no strong adhesion between the submicrometre beads and the substrate. The beads probably result from transient liquid droplet formation and progressive segregation between the original polymer (having hydrophobic character) and the oxidized products (having hydrophilic character) for compatibility reasons. Further experiments involving the wetting of the surface with water resulted in bead removal. *To our knowledge, this is the first report of the photochemical formation of submicrometre detachable beads on a polymer surface*. This behaviour of PαMS is unique and polymer specific. A comparison with PS is underway and has already indicated a somewhat different surface structure as shown in Fig. 9. Bead pattern structuring is much less pronounced. An understanding of this difference can probably be found in the different chemical and physical properties of these two polymers.

4. Conclusions

By irradiation with a polarized KrF beam in air, the PαMS surface is structured at the submicrometre level in carefully

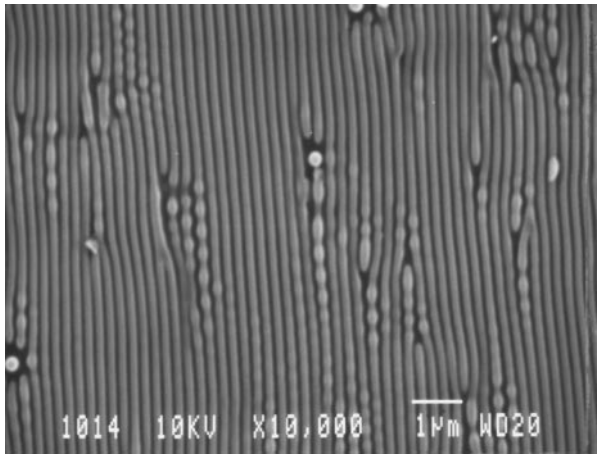

Fig. 9. PS surface structured with polarized KrF radiation ($\theta = 0°$, $\Lambda = 223$ nm) showing lines with the beginning of formation of submicrometre droplets.

controlled experimental conditions. Since the structural period is of the order of 0.5 μm, visible light diffraction and optical microscopy can be used as in situ diagnostics. The growth of the structure shows an optimum fluence of 7.2 mJ cm^{-2} in the window (6–9 mJ cm^{-2}) giving the highest structure. PαMS exhibits a unique behaviour, since its surface forms submicrometre beads periodically arranged and weakly attached to the polymer substrate. These beads, of 0.25 μm in diameter, are detached by wetting or by mechanical force (rubbing), and are formed in each line at the beginning of structuring by a thermal mechanism.

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