

Easy Way to Fabricate Nanostructures on a Reactive Polymer Surface

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The fabrication of advanced architectures in poly(glycidylmethacrylate-co-styrene) (PGMA-S) copolymers using direct laser interference patterning (DLIP) and its selective functionalization is reported. The structure features depend mainly on the laser energy used and on the styrene content in the copolymer. The topography, measured by electronic scanning microscopy, show regular and ordered arrays for the polystyrene (PS) and for the copolymers PGMA-S. The surface PS homopolymer is ablated at the position of maximum light fluence (constructive interference), while in the copolymers the surfaces swell up at the regions with maximal fluence. The styrene units are shown to absorb the laser energy giving photothermally ablated regions or promoting the chemical decomposition of acrylate units or polymer segments. In that way, DLIP provides a unique way to produce regularly ordered structures protruding or depressing from the polymer surface without altering to a large extent the chemical nature of the material. In addition, it is shown, using fluorescence microscopy, that amine-polyethyleneglycol-CdSe quantum dots (NH₂-PEG-QDs) could be spatially localized by reaction with patterned surfaces of PGMA-S. In that way, it is proven that a patterned and chemically reactive surface can be created using DLIP of PGMA-S.

Introduction

The selective functionalization of polymeric surfaces is a topic of great interest from a biological point of view. The ability to site-specific immobilize biomolecules, especially proteins, onto a solid substrate at the micro/nanoscale level is important for a variety of biological studies and applications including biosensors, studies of cell-surface interactions, cell patterning, tissue engineering, and so forth. Surface patterning is the most employed procedure to immobilize bioactive molecules such as proteins and oligonucleotides.^{1–3} Microcontact printing,⁴ microfluidics methods,^{5,6} and conventional photolithographic techniques^{1,7,8} have been employed to achieve biomolecule and cell surface patterning.

Laser-assisted patterning of polymer surfaces is a rapidly developing field that has gained considerable interest among scientists in recent years.⁹ Particularly, techniques involving large-area maskless lithography for rapid fabrication of two-dimensional polymer structures enable reduction of long processing times when large areas with high feature density patterns must be produced.¹⁰ Direct laser interference patterning (DLIP)^{11,12} permits rapid fabrication with high design flexibility.¹² The shape and dimension of the interference patterns can be adjusted by controlling the number of laser beams as well as their geometrical configuration. Furthermore, in DLIP, no masks are needed, as in optical lithography, and the structures are produced without any secondary step (e.g., etching) by the direct

interaction of the laser light with the material (e.g., photothermal, photochemical, or photophysical ablation). Materials not amenable to photopolymerization (e.g., conductive polymers, metals, or ceramics) are easily patterned using DLIP.¹³ Even more, because of the solid nature of the material, unlike in conventional optical lithography, it is possible to pattern samples with different shapes (even non planar) at any position.

Glycidyl methacrylate (GMA) is a commercially interesting functional monomer because of the presence of the epoxy reactive group, which permits a large number of chemical reactions.^{14,15} The copolymers based on GMA have great significance in advanced biotechnology by easy conversion of an epoxy group in various functional groups offering the opportunity for chemical modification of the parent copolymer.¹⁶ For example, poly(glycidyl methacrylate) (PGMA) can react with amines, thiols, phenols, proteins,¹⁷ or enzymes.¹⁸ In addition, its acidic hydrolysis produces poly(glycerol methacrylate).¹⁹ One interesting approach to improve chemical selective modification of the polymeric surface is employing DLIP over PGMA.

However, the acrylate group only can be patterned, by chain scission photolithography or ablation, using UV light (<220 nm) because the material does not absorb light above that wavelength. Great efforts have been spent in the past decades to improve the low absorption coefficient of poly(methylmethacrylate) (PMMA),^{20–22} and thus permitting its direct processing with laser light. Acrylate polymers with such characteristics would be appropriated for different applications including controlling of cell adhesion and fabrication of microlens arrays as well as micropatterning of biomolecules between others.^{21,22}

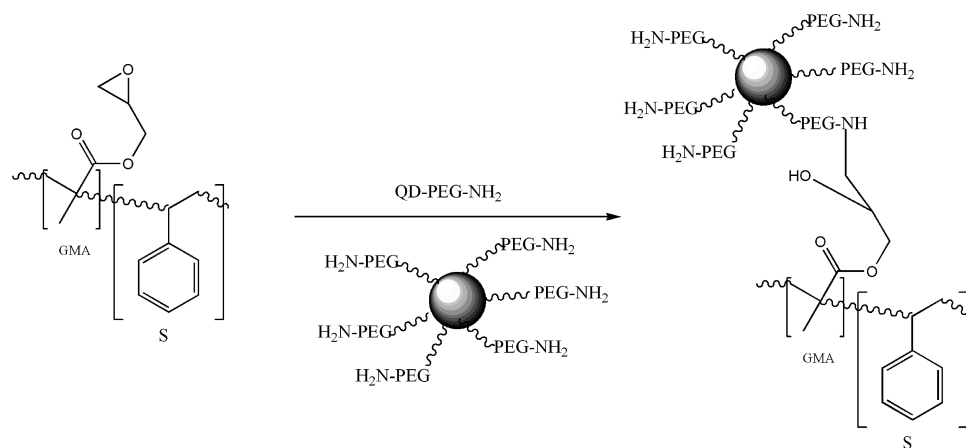
The sensitization of acrylic polymers by incorporation of a highly absorptive monomer unit (e.g., styrene) by copolymerization of the methylmethacrylate (MMA) monomer with other

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SCHEME 1: Chemical Modification of PGMA-S with NH_2 -PEG-QDs

monomers, emerges as a helpful strategy.²³ The fabrication of advanced architectures in poly(methylmethacrylate-co-styrene) (MMA-S) films using direct laser interference patterning has been reported and the influence of the copolymer composition and laser intensity on the surface topography has been studied in detail.^{23,24}

Unlike other chemically designed absorbing monomer units,²⁵ styrene has low cost; it is easily copolymerized by vinylic polymerization with different monomers, and it does not unduly affect the chemical or mechanical properties of the material. Both styrene and methylmethacrylate units are chemically inert. This is an advantage when the polymer is used only as mechanical support but is a disadvantage when chemical modification is envisaged. Then, there is the need to synthesize copolymers having a suitable absorption coefficient to be patterned and high chemical reactivity. Styrene monomer is chosen to make the polymer sensitive to laser light and the GMA to confer chemical reactivity.

In this study, we report on large area fabrication of periodic arrays on poly(glycidyl methacrylate-co-styrene) (PGMA-S) copolymer films with different compositions. The effects of polymer composition as well as laser irradiation characteristics on the surface topography are discussed. The hydrophilicity of the patterned and nonpatterned surfaces were measured by water contact angle. Finally, a proof of concept of the ability to chemically attach large entities on the patterned surface was devised by reaction of the copolymer surfaces with amine PEG semiconducting quantum dots (NH_2 -PEG-QDs), showing that the structuring process produces reactive regions surrounded by less reactive regions. The importance of this result is that other entities (adhesion proteins, enzymes, cell organelle, or complete cells) can be chemically attached to the patterned surface allowing spatial tailoring of the chemical or biological activity of the surfaces. While other methods are available to this purpose, the method described here is quite simple as it operates in air with a single 10 ns laser pulse.

Experimental Section

Materials and Methods. The monomers styrene, S (Aldrich), and glycidyl methacrylate, GMA (Aldrich), were passed through a column of activated basic aluminum oxide (Aldrich) and purged with high-purity nitrogen prior to use. 2,2'-Azobisisobutyronitrile (AIBN) from Fluka was recrystallized twice from methanol and dried under vacuum (mp = 104 °C). Tetrahydrofuran (THF) from Aldrich was distilled under nitrogen with lithium aluminum hydride. All other reagents were used without further purification.

Copolymerization Reactions. PGMA-S copolymers were synthesized in glass ampoules sealed with rubber septa in bulk ($3 \text{ mol} \cdot \text{L}^{-1}$) using AIBN as an initiator. Dissolved oxygen was removed from the reaction solution by nitrogen purging for 30 min prior to immersion in a water bath at 50 ± 0.1 °C. After a specified length of time, each ampoule was removed from the water bath, and the reaction was stopped with 0.5 mL of a 10 wt % solution of hydroquinone in THF. Ether/heptane mixtures were used to isolate the copolymers. All samples were purified by reprecipitation with THF as the solvent and ether-heptane mixtures as the precipitant and then dried under vacuum in the presence of phosphorus pentoxide until a constant weight was attained. The chemical composition of copolymers was estimated by nuclear magnetic resonance (NMR).

Amine-PEG-QDs -PGMA-S Reaction. The copolymers patterned and nonpatterned were modified using a solution 10^{-5} M of NH_2 -PEG-QDs in water. The reaction was carried out at room temperature during 1 h. The modified film was gently raised with distilled water (See Scheme 1).

Laser Interference Experiments. A high-power pulsed Nd:YAG laser (Quanta-Ray PRO 290, Spectra Physics) with a wavelength of 266 nm was used for the laser interference experiments. The pulse duration was 10 ns and only 1 laser pulse was used in each experiment. To obtain the line-like periodic patterns, the fundamental laser beam was split into two sub-beams and guided by mirrors to interfere on the sample surface. The samples were irradiated with laser fluences up to approximately $500 \text{ mJ} \cdot \text{cm}^{-2}$. All experiments were conducted in air at normal conditions of pressure and temperature.

Samples Characterization. ^1H NMR spectra were recorded at 300 MHz on a Varian Inova 300 spectrometer at 45 °C with deuterated chloroform (10 wt % solutions).

Fourier transform infrared spectra (FTIR) of the copolymers in the transmission mode were obtained in KBr pellets using a Perkin-Elmer System 200 spectrometer with a 4 cm^{-1} resolution.

Raman spectra were obtained with a Renishaw invia Raman microscope. The excitation line was provided by a 320 mW diode array laser at 785 nm. The laser beam was focused through a $50\times$ long-working objective (0.75 NA). The diameter of the laser beam spot on the sample surface was $2 \mu\text{m}$.

Surface topography of the irradiated samples was characterized using white light interferometry (WLI). The samples were further analyzed by scanning electron microscopy using a Philips XL30 SEM equipment working at 25 kV: the samples were covered with a thin Au/Pd overlayer by physical vapor deposition (PVD).

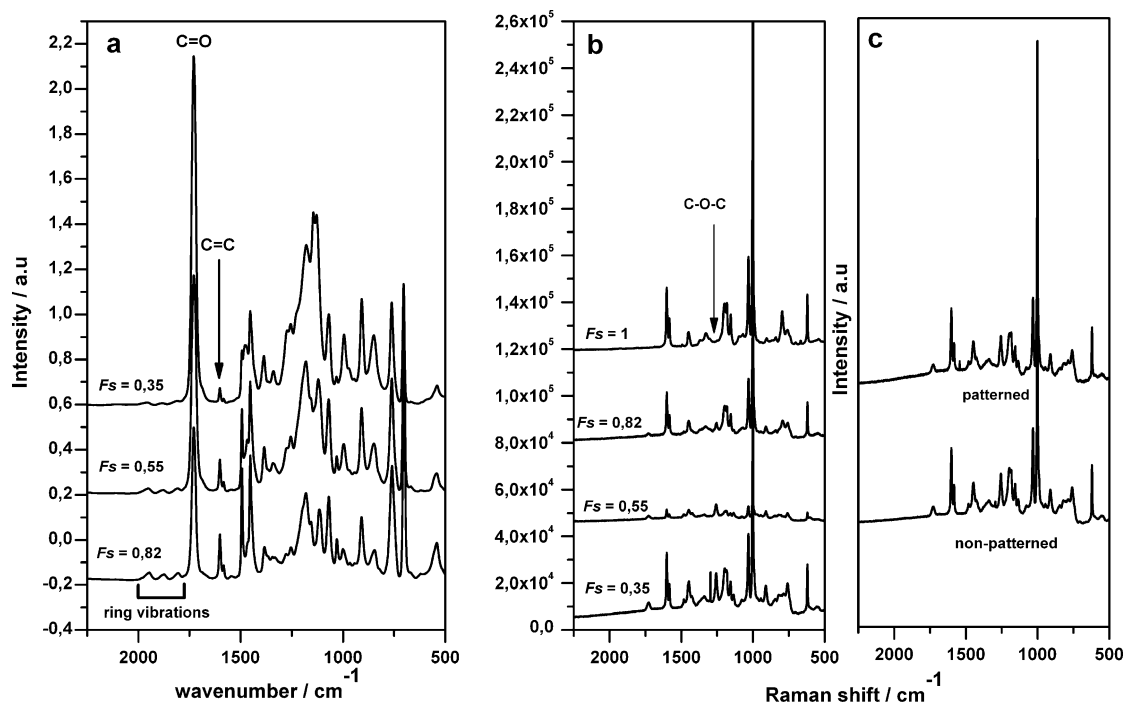


Figure 1. FTIR (a) and Raman (b) spectra of several PGMA-S copolymers. A comparison between patterned and nonpatterned zones for PGMA-S $F_S = 0.35$ (c).

A computer controlled microscope Intel QX3 was used for measurement of contact angle by setting flat polymer pieces on a manually controlled tilt table, illuminated from behind with a white light source and recording, with the microscope in horizontal position, the shape of water drops ($3\ \mu\text{L}$) standing still on the surface using a $60\times$ objective. The pictures were analyzed using “drop analysis” software.²⁶

Furthermore, both nonpatterned and patterned PGMA-S copolymer surface were examined under a fluorescence microscope (Axiophot, Zeiss, Germany) using a color camera (Axiocam, Zeiss, Germany) driven by Axiovision 4.3 software. The excitation and emission filters used were BP 436 FT and 460 LP 470 (Zeiss, Germany), respectively.

Results and Discussion

The PGMA-S copolymers were characterized by FTIR and Raman (Figure 1). FTIR in the transmission mode for the PGMA-S copolymers are shown in Figure 1. As the concentration of GMA in the copolymer increases the signal of the bands associated to the glycidyl methacrylate group increases, and the intensity of those corresponding to styrene decreases (Figure 1a). For example, a remarkable increase in the C=O stretching of the carboxylate group at $1730\ \text{cm}^{-1}$ can be observed. In addition, the band corresponding to the C=C stretching of aromatic rings, around $1606\ \text{cm}^{-1}$, and those associated to ring vibrations in styrene units ($2000\text{--}1750\ \text{cm}^{-1}$) decrease.

The Raman spectra of the copolymers shows the remarkable increases of a band centered at $1256\ \text{cm}^{-1}$, which correspond to the C–O–C stretching of the epoxy group in GMA units (Figure 1b). Raman spectroscopy also allows us to analyze the bands in both the patterned and the nonpatterned surfaces. However, the patterned surface shows identical spectrum to that of the nonpatterned one, showing that the process of DLIP does not produce the hydrolysis of labile epoxy group (Figure 1c). Instead, it seems that the surface is physically ablated, leading to change in the topography by elimination of the first layer of the copolymers. The copolymer composition was accurately

TABLE 1: Molar Feed Composition (f_s), Experimentally Determined Copolymer Composition (F_s), and Conversion for the Free Radical Copolymerization of S and GMA at $50\ ^\circ\text{C}$ in Bulk

f_s	F_s	conversion (wt %)
0.9	0.82	9.4
0.7	0.55	5.3
0.3	0.35	7.4
0.1	0.18	7.4

determined with the help of ^1H NMR spectra by comparing the integrated intensities of the signals of aromatic protons of the styrene (5H, 6.4–7.2 ppm) with the peaks of the well-pronounced bands of 2,3-epoxypropyl group –COO–CH₂ (2H, 3.6–4.4 ppm; not shown). The variation of copolymers composition (F_s) is shown in Table 1.

A copolymer reactivity plot, Figure 2, shows the relationship between the feed ratio and the copolymer composition. The data can be fitted with a copolymerization reactivity eq 1 because the low conversion allows exact fitting without compositional drift.²⁷

$$F_s = \frac{f_s(1 + [r_2 - 1]f_s)}{(r_1 + r_2 - 2)f_s^2 + 2(1 - r_2)f_s + r_2} \quad (1)$$

The calculated reactivity coefficients are $r_1 = 0.32$ and $r_2 = 0.475$. The values are in the order of those previously measured for copolymerization of styrene and other arylates.²⁸

The important point is that the reactivity of the comonomers is not the same (see dashed line in Figure 2), except for an azeotropic feed ratio²⁸ of approximately 0.4. Therefore, the copolymer backbone will be constituted by segments of styrene and GMA units and not by an alternate copolymer.

The surface topography of the fabricated periodic structures in different copolymers with specific monomer composition was investigated. A two laser beam configuration was used to obtain

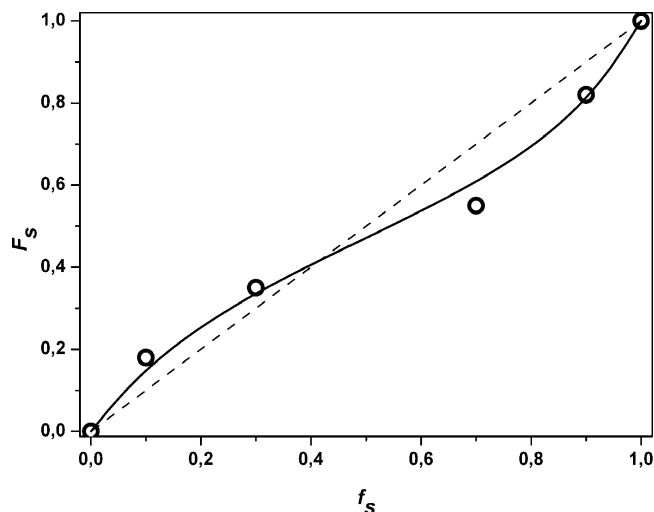


Figure 2. Plot of the copolymer composition in styrene (F_S) as a function of the feed ratio (f_S). The full line represents a fitting using eq 1 while the dashed line represents the case where the reactivity of both monomers is the same.

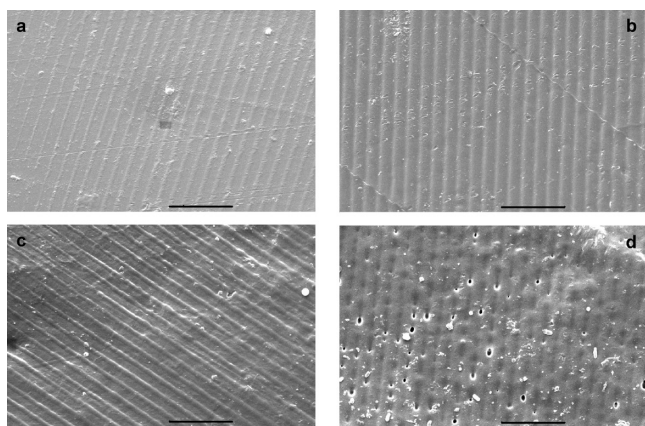


Figure 3. SEM images PS and different PGMA-S surfaces irradiated using a laser fluence of $468 \text{ mJ} \cdot \text{cm}^{-2}$. Copolymer of composition $F_S = 1$ (a), $F_S = 0.82$ (b), $F_S = 0.55$ (c), and $F_S = 0.35$ (d). Scale bar = $10 \mu\text{m}$.

line-like interference patterns. In all cases, the utilized wavelength was 266 nm because of the high absorption coefficient of PS at this wavelength.²⁹ The period measured using WLI (not shown) is $2.1 \mu\text{m}$ for all of the polymers.

Figure 3 shows scanning electron micrographs of PS and PGMA-S copolymers irradiated at the same laser fluence ($468 \text{ mJ} \cdot \text{cm}^{-2}$). For PS, well-ordered structures are observed, and in the region of the maximum fluences, it can be observed that the surface is depleted (Figure 3a). The average line width of the ablation zones is around $1.7 \mu\text{m}$. For the PGMA-S with the highest content of styrene ($F_S = 0.82$), the behavior is quite similar to PS (Figure 3b). However, the average linewidth of the ablated zones diminishes to 790 nm . This decrease can be attributed to the lower absorption coefficient of PGMA-S compared with that of PS due to the presence of approximately 18% of the non-absorbing monomer, GMA. However, despite the presence of the GMA monomer, the copolymer has a behavior similar to PS, while a reactive group has been incorporated. Nevertheless, increasing the amount of GMA produces a material with a different behavior from that observed for PS. For example, for PGMA-S copolymer with $F_S = 0.55$, the surface expands in the region of the maxima laser fluences (Figure 3c), and for the copolymer with $F_S = 0.35$, it seems

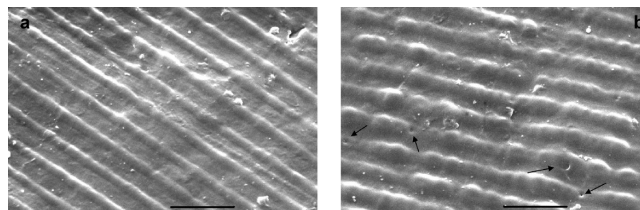


Figure 4. SEM images of GMA-S copolymer ($F_S = 0.55$) irradiated using two different laser fluences, (a) $468 \text{ mJ} \cdot \text{cm}^{-2}$ and (b) $548 \text{ mJ} \cdot \text{cm}^{-2}$. Arrows in the right image indicate the holes produced by removal through volume bubble formation. Scale bar = $5 \mu\text{m}$.

that the structure inflates first and then it collapses producing holes (Figure 3d). This is likely to be due to the chemical decomposition of GMA units or segments promoted by the thermal energy produced by nonradiative decay of the styrene units. Beyond the different behavior observed especially for the copolymer with the lowest content of PS, the results indicate that most of PGMA-S can be patterned using the same laser fluence range employed for PS due to the addition of styrene monomer units with a high absorption coefficient.

We have also analyzed the effect of the laser fluence on the surface topography. We have chosen the copolymer with $F_S = 0.55$. Figure 4 shows the scanning electron micrographs of PGMA-S with $F_S = 0.55$ of styrene irradiated at two different energies. The copolymer shows a dependence on the laser energy similar to copolymers of methylmethacrylate-co-styrene, and the irradiated surfaces swell up because of the formation of microbubbles probably as a result of the depolymerization in the degradation process.^{23,24} At higher laser intensities, the bubbles release from the surface forming a nonperiodic micropored structure. In these cases, probably the high content of the acrylic monomer makes the copolymer behave as PMMA which ablates through subsurface superheating, meaning that the material heats above its softening point below the surface producing acoustic waves due to material's inherent elasticity.^{23,28}

Taking into account the different chemical nature of the monomers, the wettability of the surfaces was investigated using water contact angle measurements (Figure 5).

It can be seen that the value of the contact angle (Figure 6) does not significantly change as the content of styrene in the copolymer decreases. By taking into account this result, it is possible to suggest that the chemistry of the surface does not alter significantly the wettability.

On the other hand, when the surface is patterned, the material shows a different behavior. For PS, the contact angle increases upon irradiation, making the irradiated surface more hydrophilic than the nonirradiated one. It is well-known that the contact angle of the hydrophobic surfaces increases with roughness³⁰ due to the formation of air pockets in the trenches below the surface (see Figure 5).

The same behavior is observed for the copolymer with highest content of styrene units ($F_S = 0.82$). However the difference between nonpatterned and patterned is higher, while the width of the trenches is smaller ($0.79 \mu\text{m}$ vs $1.7 \mu\text{m}$; see Figure 3). It is likely that some chemical modification of the GMA units occurs leading to the elimination of polar epoxy groups and making the surface more hydrophobic. The Raman spectroscopy of the surface does not show a significant difference between the patterned and the nonpatterned PGMA-S. However, it will be shown (see below) that the reactivity of the surface is affected by the ablation process.

For the copolymer with lowest content of styrene ($F_S = 0.35$), a different behavior can be observed. The contact angle is not

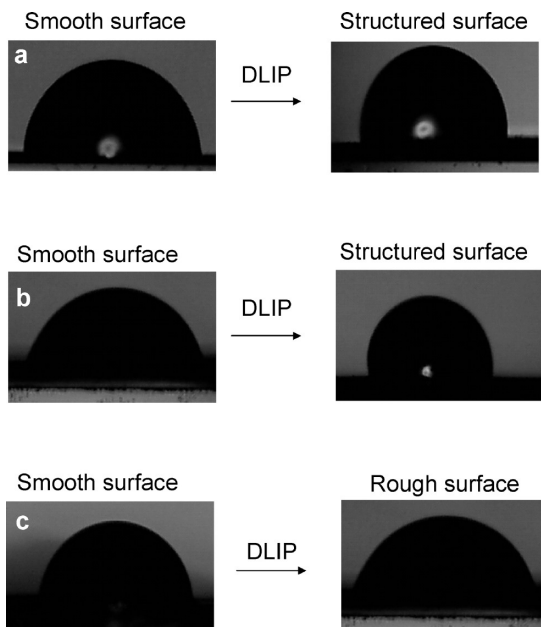


Figure 5. Photographic record of water drops onto polymeric surfaces, revealing the effect of copolymer composition and laser structuring on water contact angle. (a) PS, (b) PMGA-S $F_s = 0.85$, and (c) PMGA-S $F_s = 0.35$.

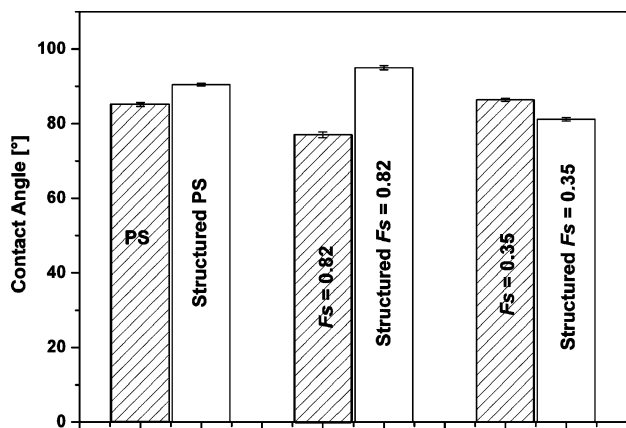


Figure 6. Contact angle measurement of patterned and nonpatterned GMA-S copolymers, obtained from Figure 5.

affected by the laser irradiation, while a clear structuring occurs. This is likely due to the fact that laser irradiation does not lead to a regular structure but to a randomly rough surface. Therefore, the air pockets do not form or are too small to affect the wettability of the surface.

It is widely known that GMA monomer and polymers can be easily modified by chemical reaction with the highly reactive epoxy group. In that way, large biological entities (enzymes, antibodies, etc.) can be attached. As a proof of concept of the chemical attachment of large entities, amino decorated fluorescent quantum dots (NH_2 -PEG-QDs), which can be easily localized by fluorescence microscopy, are reacted with PMGA-S surfaces. Figure 7 shows the fluorescence micrographs obtained after modification of both nonpatterned (Figure 7a) and patterned (Figure 7b) PMGA-S surfaces ($F_s = 0.82$). As it can be seen, the QDs are attached to the polymer surface in both cases. However, in Figure 7b, a regular ordered distribution of NH_2 -PEG-QDs on the top of the lines is observed. Therefore, it is likely that the physical structuring by DLIP not only changes the topography but also changes the chemistry of the PMGA-S surfaces, as it is reflected in the reactivity and wetting ability.

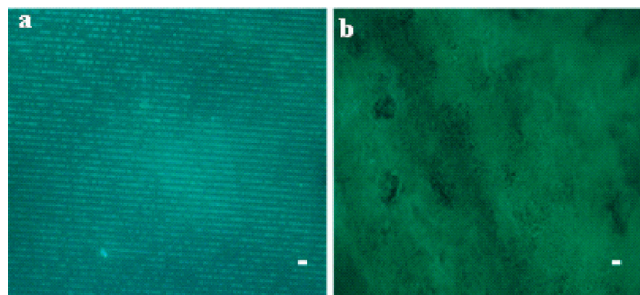


Figure 7. Fluorescence microscopies of surface modified with NH_2 -PEG-QDs: (a) patterned surface and (b) nonpatterned surface for copolymer $F_s = 0.82$. Scale bar = $2 \mu\text{m}$.

On the basis of these results, it can be suggested that the immobilization of biological compounds (adhesion proteins, enzymes, growth factors) on a patterned surface can be easily made by the method described above leading to polymer surfaces useful for biotechnological applications.

Conclusions

A simple method to produce ordered structures of a highly reactive polymer was described. Regular and ordered features have been produced by laser interference patterning using a single 266 nm laser pulse, in air. The pattern shapes depend on the laser fluence and the copolymer composition. At high laser fluences and with a high content of styrene units, the surface is ablated by the laser leaving trenches or holes. At low laser fluences and medium content of styrene units, the irradiated surfaces swell up producing lines or points protruding from the surface. At high laser fluences and low content of styrene units, the irradiated surface swells and explodes leaving a rough surface.

The patterned surfaces display different wetting properties with respect to the nonpatterned surfaces. The patterned surfaces are more hydrophobic than the untreated ones, because of the formation of air pockets below the water drop.

The epoxy groups in GMA can be used to anchor amine covered NH_2 -PEG-QDs on the copolymer surface. Even more, we have shown that the QDs can be selectively attached on the nonirradiated zones, leaving the irradiated zones unmodified.

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