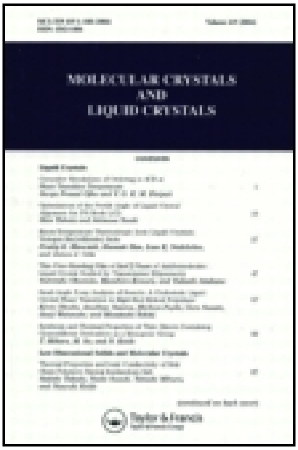

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Azo-Containing Polymer Brushes: Photoalignment and Application as Command Surfaces

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Azo-Containing Polymer Brushes: Photoalignment and Application as Command Surfaces

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A brush polymer containing photosensitive mesogenic side chains has been directly synthesized on glass substrates by a grafting method involving polymerization of a metacrylic azobenzenic monomer under Atomic Transfer Radical Polymerization (ATRP) conditions. Brush polymer surfaces, with respect to more traditional films, are resistant to solvents and to high temperatures due to the covalent bonds between chain and substrate, which stabilizes the film morphology. The peculiar characteristics of the present polymeric brushes, namely the intrinsic in-plane orientation of the mesogenic units located in the side chains, together with the possibility of a fine control on the structure, make them very attractive for application as command surfaces.

We then employed such brushes as photo-controllable command surfaces in twisted/planar switchable cells filled with a low molecular weight liquid crystal and we characterized the molecular order at interface by means of confocal polarized Raman microscopy.

Keywords: ATRP; azobenzene; confocal polarized Raman spectroscopy; optical command surface; polymeric brush; polymeric liquid crystals

INTRODUCTION

The production of surfaces with anisotropic anchoring properties is of fundamental importance in the fabrication of liquid crystals (LC)

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based electro-optic devices. The surface-mediated alignment of LC involves the production of an anisotropic surface, which can be obtained by the traditional mechanical rubbing or by more recently introduced optical methods (for a review see [1]), based on several kinds of photoinduced reactions, such as photoaligment, photocrosslinking or photoadsorption, many of which have the advantage of being switchable. In particular, optical methods appear more attractive with respect to the rubbing technique since light can be focused and used to develop microstructures where the LC director orientation varies at high spatial resolution, as required for construction of complex electro-optic devices. The surface-mediated LC photoalignment has been demonstrated in the literature using molecular layers (or polymeric film) containing different photoreactive groups: azoaromatics [2–5], cinnamates [6,7], and coumarins [8].

Among these materials, the azobenzene derivatives exhibit excellent photochromic properties such as reversibility, stability, fatigue resistance and they have been extensively studied in a variety of different systems [9]. The first application of an azobenzene monolayer as command surface in a LC cell reports the photo-triggered switch of the nematic director orientation between the homeotropic and planar configuration, obtained by the photoisomerization of the azo-dyes with unpolarized light [2], while successively it has been shown that such command surfaces allows also the control of the in-plane LC orientation trough the photoalignment of azobenzene mesogens with polarized light [5]. Polarized illumination induces a reorientation of azobenzene moieties perpendicular to the electric field of the incident light with a subsequent in-plane easy axis reorientation of the LC at the interface. For this application, polymeric brushes with mesogenic side chains have been recently proposed as the most suitable system [10]. In contrast with the traditionally employed polymeric films produced by Langmuir Blodgett or spin coating, side chain polymeric brushes display a unique layer structure with the mesogenic units oriented parallel to the substrate. Such a structure appears particularly suitable since it provides a higher and more anisotropic planar anchoring. Moreover polymeric brushes, with respect to traditional films, are resistant to solvents and to high temperatures due to the covalent bonds between chain and substrate, avoiding the dissolution of polymeric layer in LC and stabilizing the film morphology. Furthermore, their synthesis can be achieved by use of a controlled polymerisation procedure such as surface-initiated atom transfer radical polymerisation (ATRP) [11–13], for a fine tuning of brush length.

Herein, we report the preparation of a polymeric brush containing azobenzene and its application as command surface in a LC cell.

The assembled device has been micropatterned with laser illumination and the induced LC order parameter has been measured on the command surface by confocal polarized Raman micro-spectroscopy.

MATERIALS AND METHODS

We have prepared a grafted azopolymer, depicted in Figure 1, obtained by ATRP onto silica substrate of monomer 4-ω-methacryloyloxyhexyloxy-4′-ethoxyazobenzene (M6A) (Fig. 1) which has been synthesized as previously reported [14]. The polymeric grafted brushes

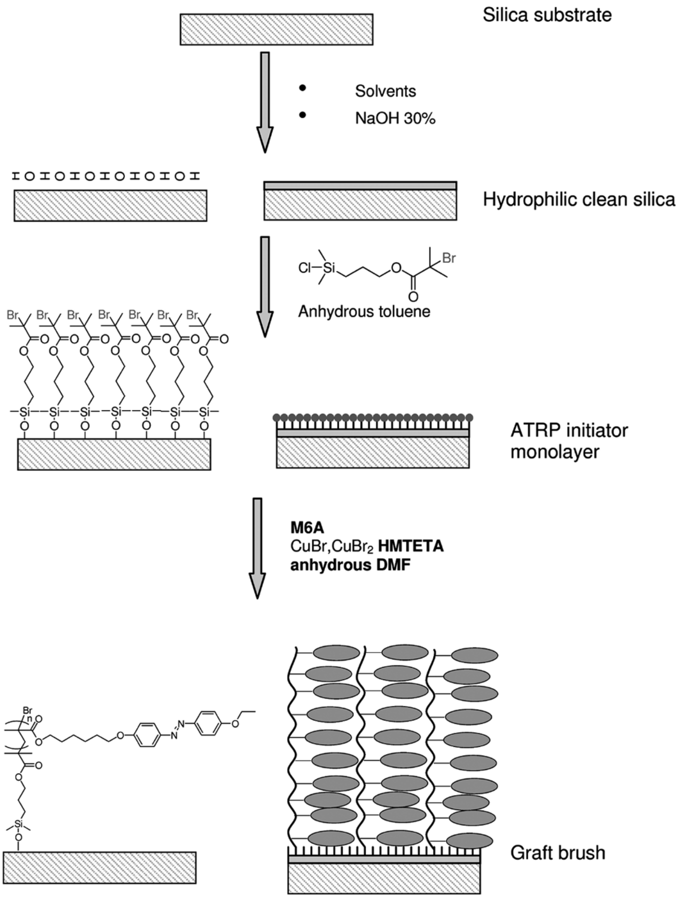

FIGURE 1 Synthetic procedure and structural formula of the investigated grafted brushes onto silica substrates.

were synthesized (as show in Fig. 1) from bromine-modified substrates by surface-initiated ATRP procedure.

Preparation of silica substrates: silica substrates were cleaned in a sonicator for 5 minutes with several solvents of increasing polarity (toluene, dichloromethane, acetone, methanol, water and 1% v/v soap solution in water) in order to remove any trace of organic deposit and washed with a large amount of water. Cleaned glass substrates were then activated by a 30% w/w aqueous solution of NaOH, rinsed with a large amount of milliQ water, dried under nitrogen atmosphere, put in a slenk tube, stored under high vacuum for four hours in order to remove adsorbed gases and humidity and finally the flask was purged with anhydrous nitrogen.

Preparation of bromine-modified substrates: the ATRP surface initiator, 3-(chlorodimethylsilyl) propyl 2-bromo-2-methylpropanoate, was synthesized according to a previously published method [15].

The immobilization of the initiator onto the silica substrates was directly achieved in the aforementioned slenk tube in nitrogen atmosphere adding up a 10 mmol/L solution of the surface ATRP in anhydrous toluene and then let react overnight at room temperature [16].

In order to remove the unreacted initiator, the functionalized substrates were cleaned several times with dry toluene, dried under nitrogen atmosphere and stored at room temperature under high vacuum.

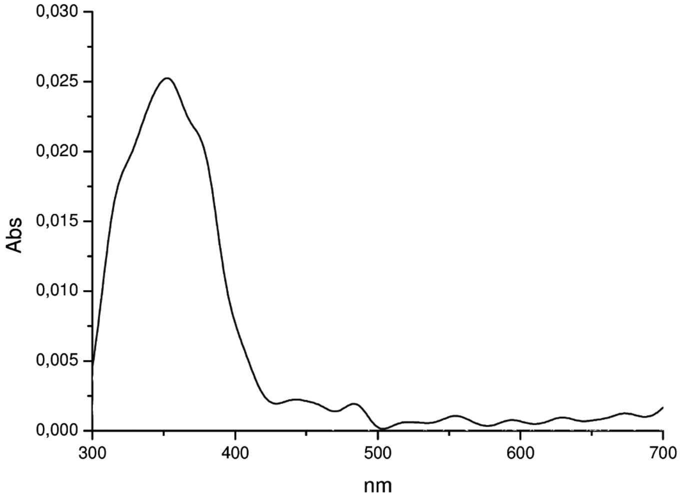

FIGURE 2 UV-Vis absorption spectrum of an azoaromatic polymeric brush obtained after 4 hours polymerization time graphed on both sides of the silica substrate.

Surface initiated ATRP: the graft polymerizations of M6A were carried out in anhydrous DMF solution for 4 hours using CuBr as catalyst, $CuBr_2$ as deactivator [17] and 1,1,4,7,10,10-hexamethyltryethylentetraamine (HMTETA) as ligand with molar ratio of Monomer/CuBr/$CuBr_2$/HMTETA = 50:1:0, 1:2, 2 and a M6A concentration of 0,25 mol/L.

After this desired polymerization time, in order to remove the unreacted monomer, the grafted substrates are washed several times with distilled THF and finally dried under nitrogen flow.

The thickness of the polymeric brush was then measured either by extinction null ellipsometry operated at $\lambda = 633$ nm, or by UV-vis spectroscopy, resulting in a typical thickness of 5 nm for a brush of M6A after 4 hours of polymerization time. An example, the UV-vis absorption spectrum of a grafted polymeric film, is reported in Figure 2.

PREPARATION AND CHARACTERIZATION OF LC CELL

The prepared polymeric brushes substrates have been employed for the fabrication of photo-switchable twisted/planar LC cells filled with the low molecular weight nematic pentyl-cyanobiphenyl (5CB). The cells have been produced using two different boundary glass walls, namely a *reference* and a *command* surface. The reference substrate has been coated with a polyimide layer, which has been mechanically rubbed in order to induce a strong homogeneous planar orientation, while the azo-polymer brush provides the photo-controllable command surface. The substrates have been assembled with a 10 μm spacer and filled with 5CB in its isotropic phase at 45°C. After slow cooling (−0.5°C/min) to room temperature, the cells display a planar alignment along the direction imposed by the reference surface. Twisted or planar structures have been then achieved by aligning the azobenzene mesogens on the command surface, respectively perpendicularly or parallel to the rubbing direction of the reference substrate, by mean of polarized illumination with the 488 nm Ar/Kr^+ laser line. The images in Figure 3 report an example of micropatterning in a cell prepared in the twisted configuration by macroscopic polarized irradiation and then locally (20 μm) reverted to planar by focused illumination with perpendicular polarization. We compared, trough polarizing optical microscopy, the photoinduced structures thus obtained with those produced in the same experimental condition in cells where the command surface was provided by a spin coated layer of polymers synthesized from the same monomer. We assembled the cells employing azo-polymers of different molecular weight and geometry (linear-star) [18,19] and the photo-induced patterning resulted not

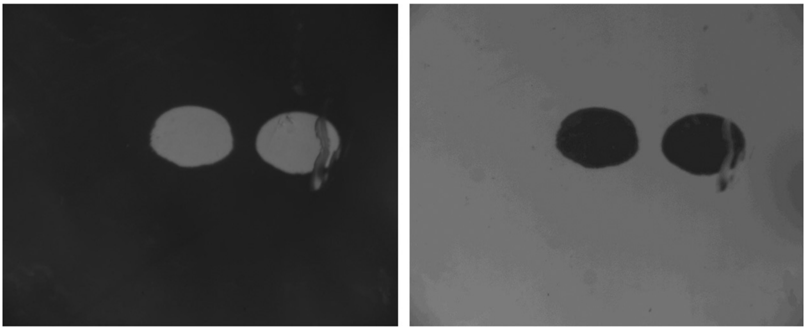

FIGURE 3 Polarizing microscopy images of 20 μm diameter planar structures in a twisted cell. Left and right image has been acquired respectively with parallel and crossed polarisers.

clearly visible under microscope. On the contrary the structures produced on azo polymeric brush cells display a high contrast (in the order of 1:100) and appear uniform either on macroscopic or microscopic scale, without LC defects like disclination lines.

We then proceeded with the Raman characterization of the LC order at the polymeric brush interface using the same confocal microscope employed for the patterning. The laser emission has been set to the 647 nm line, outside the azobenzene absorption band, in order to avoid further photoinduced effects. The spectra have been collected in the back scattering geometry with a Jobin Yvon-Horiba T64000 spectrometer equipped with a liquid N_2 cooled CCD detector. The polarized micro-Raman study has been carried out measuring the 5CB peaks intensities as a function of the incident polarization and the analyzer directions along the two orthogonal axis V and H, respectively parallel and perpendicular to the nematic director. More specifically, the measurement consists of the acquisition of the peak intensity for the four possible geometries I_{VV}, I_{VH}, I_{HH}, and I_{HV}, where the first index refers to the incident polarization and the second to the analyzer direction. In Figure 4 is reported the characteristic Raman peak of 5CB corresponding to the symmetric stretching of the benzene rings ($1605\,cm^{-1}$) measured in the four geometries on the pristine cell. The selected $1605\,cm^{-1}$ mode provides a suitable Raman probe for the orientation measurement since the main axis of the vibration is parallel to the central rigid part of the molecule, namely along the main axis of the mesogenic group. Such vibration is also particular suitable for the order parameters calculation since is uniaxial and strongly polarized with a ratio of the diagonal terms of the molecular polarizability tensor close to zero ($\alpha_H/\alpha_V = 0.045$ [20]). The high anisotropy of the

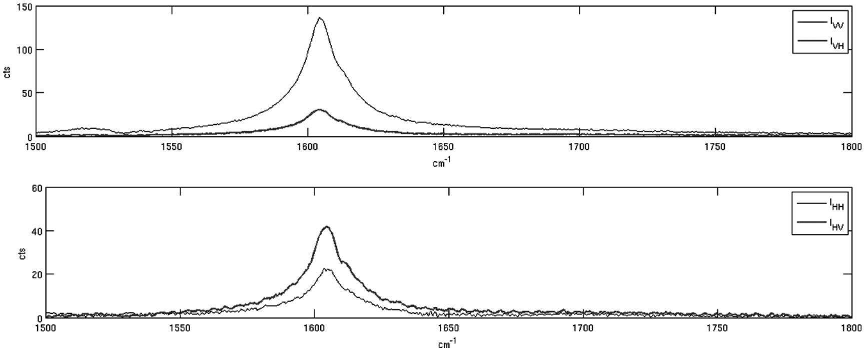

FIGURE 4 Raman peak of 5CB corresponding to the symmetric stretching of the benzene rings ($1605\,\mathrm{cm}^{-1}$) measured in the four geometries I_{VV}, I_{VH}, I_{HH}, and I_{HV}.

selected vibration allows to obtain the order parameters P_2 on the basis of scattering anisotropies R_1 and R_2 defined as $R_1 = I_{VH}/I_{VV}$ and $R_2 = I_{HV}/I_{HH}$, by the calculation of the second average cosine powers of the molecular orientation θ trough the approximated formula [21]:

$$\left\langle (\cos\theta)^2 \right\rangle = \frac{3R_2(2R_1+1)}{8R_1+3R_2+12R_1R_2}$$

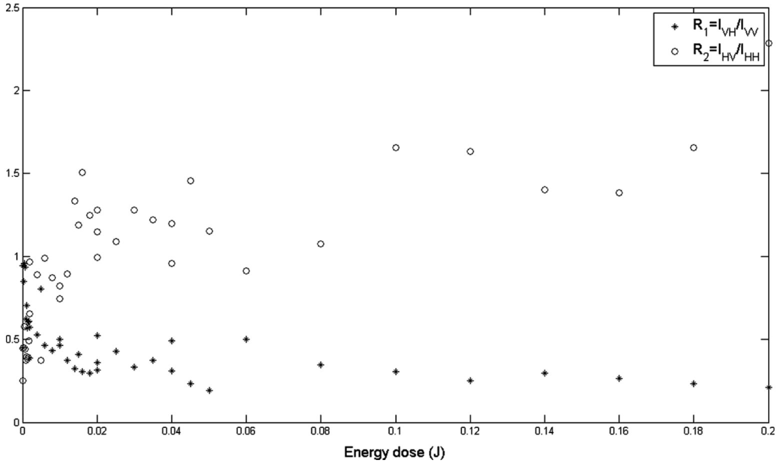

FIGURE 5 Scattering anisotropies R_1 and R_2 measured on the illuminated areas as a function of the energy dose of the pump beam.

The scattering anisotropies R_1 and R_2 have been measured on the pristine surfaces and on the illuminated areas as a function of the energy dose of the pump beam. Twisted microstructures (20 μm diameter) have been photo-induced on the original planar cell varying both pump power (200 μW-20 mW) and exposure time (1–10 sec). The scattering anisotropies as a function of power multiplied by exposure are reported in Figure 5. The data show a threshold energy about 0.5 mJ where R_2 becomes greater than R_1 and saturation about 100 mJ where the parameters remain roughly constant. The average order parameter P_2 calculated at the saturation energy dose results 0.53 which is increased respect to the original value $P_2 = 0.48$ and of the same order of that measured on the reference rubbed substrate of 0.52.

CONCLUSION AND FUTURE WORK

We have synthesized polymeric brushes containing an azobenzene side chain for application as command surface in a photo-switchable twisted/planar liquid crystals cell. The assembled device shows excellent properties in terms of uniformity and molecular order, with a controllable order parameter on the command surface which can be as high as that obtained by the traditional rubbing method. These preliminary results suggest the undertaking of a study aimed at the optimization of the command surface through the tuning of the brush parameters such density, length, chemical composition and to employ the polymeric brush as a tool for investigation on the solid-LC interface.

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