

## Light responsive thin films of micelles of PS-*b*-PVP complexed with diazophenol chromophore

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 Nanotechnology 25 065601

(<http://iopscience.iop.org/0957-4484/25/6/065601>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 200.0.182.38

This content was downloaded on 19/06/2014 at 17:12

Please note that [terms and conditions apply](#).

# Light responsive thin films of micelles of PS-*b*-PVP complexed with diazophenol chromophore

Luciana M Saiz, Patricia A Oyanguren, María José Galante and Ileana A Zucchi

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina

E-mail: [ileanazu@yahoo.com.ar](mailto:ileanazu@yahoo.com.ar)

Received 4 September 2013, revised 8 November 2013

Accepted for publication 25 November 2013

Published 16 January 2014

## Abstract

We have incorporated push–pull azobenzene units into diblock-copolymer micelles by supramolecular assembly. Specifically, we encapsulated a phenol-functionalized chromophore, DO13, within PS-*b*-P4VP micelles in toluene by means of H-bond interactions developed between DO13 molecules and pyridine groups of P4VP block. The solutions were spin-coated onto glass substrates resulting in multi- or mono-layered thin films of micelles with P4VP(DO13) core and PS corona. We show that the use of DO13 as a building block of micellar aggregates allowed us to manipulate the developed nanostructures. Spherical to cylindrical micellar transition was found when we increased the degree of chromophore complexation. Also, it was found that the polymer concentration in the solution plays an important role in determining the micellar nanostructures. The chain extension and change in composition of the P4VP core in the presence of the chromophore may be responsible for the structural changes observed in the micelles.

The optical properties of the thin films have been investigated focusing on the effect of the micellar morphology over the photoinduced birefringence. The optical anisotropy ( $\Delta n$ ) increased with respect to the analogous homogeneous system P4VP(DO13), indicating that the protective micelle environment can enhance the optical properties of the embedded chromophores significantly. Furthermore, we show very interesting new results in which we have related changes in optical properties to the film morphology (spheres to cylinders). This can be exploited for producing optical devices having improved optoelectronic properties and stability.

Keywords: azo polymers, block-copolymer, micelles, photoinduced birefringence, supramolecular interactions

 Online supplementary data available from [stacks.iop.org/Nano/25/065601/mmedia](http://stacks.iop.org/Nano/25/065601/mmedia)

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Azobenzene-containing polymers have been extensively investigated because of the unique response of the azobenzene (azo from now on) moiety to light fields [1]. Its key feature is the efficient and reversible isomerization between a thermally

stable *trans*-state and a metastable *cis*-state. Excitation with linearly polarized light of appropriate wavelength can be used to induce large and stable in-plane anisotropy in initially isotropic azobenzene-containing polymers.

Diblock copolymers (DBC) composed of two different polymers form nanometer-sized micelles consisting of a

soluble corona and an insoluble core in a selective solvent for one of the blocks [2]. Most common micellar structures are spherical, however other specific micellar aggregates like cylindrical micelles, vesicles, crew-cut micelles and micelles with multi-compartments can also be prepared by controlling various factors such as composition, ionic strength, polymer concentration, sample preparation conditions and solvent selectivity [3–10]. Micelle structures are very attractive since they can incorporate organic molecules, and metal and oxide nanoparticles, enabling one to engineer hybrid nanocomposites. The use of micelle structures can protect the encapsulated species and may even enhance the interaction among the species themselves.

In consequence, it can be expected that bringing the appealing features of azo chromophores and DBCs together in micellar aggregates could result in interesting systems, taking into account the need for new materials with specific functionalities appropriate for emerging technological applications.

One way to incorporate the azo unit into DBC micelles is by supramolecular assembly. Supramolecules offer advantages over the covalently linked analogues, since different functionalities can be easily incorporated, avoiding steps related to the complicated organic synthesis required for each combination of a polymer and a small molecule. Supramolecular assembly has been extensively studied in the case of complexes based on homopolymers and azo chromophores like Disperse Red 1 (DR1) [11], 4-nitro-4'-hydroxyazobenzene (NHA) [12], and Disperse Yellow 7 (DY7) [13], since the hydrogen bonding allows the introduction of large amounts of dye without aggregation, and consequently the enhancement of the optical properties of the resulting polymers.

DBC-based supramolecules are prepared by attaching small molecules to one of the DBC blocks [14, 15]. Tunable morphologies are readily accessible using a single DBC, either by varying the stoichiometry between the small molecules and the DBC or by redistributing the small molecules between the two microdomains using an external stimulus, like heat [14].

Poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP) is a class of nonionic, amphiphilic DBC which has been of great interest in the study of micellar properties because of its ability to develop H-bond interactions through the pyridine group. It has been a frequently studied DBC as a template for fabricating metal nanoparticles (NPs) or quantum dots from their micellar thin films [16, 17], as nanoreactor whereby metals can be loaded via complexation with the nitrogen of the pyridine and then reduction which leads to the formation of nanoparticles in the core of micelles [18–20], or to encapsulate NPs within micelle cores through directed supramolecular assembly [21].

In recent years, the preparation of supramolecular self-assembly of PS-*b*-P4VP with an addition of small molecules which can form hydrogen bonds with the P4VP block has received a good deal of attention. 3-pentadecylphenol was extensively used as a powerful modifier to manipulate the orientation in PS-*b*-P4VP thin films [22–24], Coumarin dye [25] and DR1 [26] were complexed looking for improvements in their fluorescence emission, and likewise 6-[4-(4'-cyanophenylazo)phenoxy]hexanoic acid, to get azobenzene-containing polymer materials with low chromophore content, of interest in optical application [27].

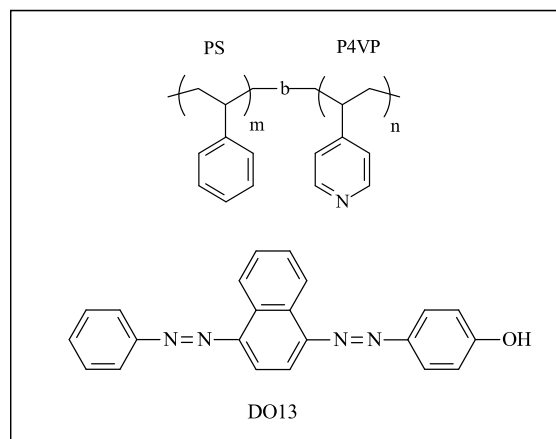


Figure 1. Chemical structures of the PS-*b*-P4VP and DO13.

In this work, with the aim of synthesizing films with improved optoelectronic properties, we have encapsulated a phenol-functionalized chromophore (Disperse Orange 13, DO13) within PS-*b*-P4VP micelles in toluene by means of H-bond interactions developed between DO13 molecules and pyridine groups of P4VP block. Multi- or mono-layered thin films of micelles with P4VP(DO13) core and PS corona were developed conjugating the fascinating characteristics of supramolecular assembly, PS-*b*-P4VP micellar nanostructures and azopolymers in a single film. The selected chromophore, DO13, offers an extra advantage from the point of view of the optical properties, since it bears two isomerizable azobenzene units. The polymeric systems modified with bisazobenzenes are known to give rise to higher and more stable photoinduced anisotropy than the corresponding azobenzene polymers functionalized with monoazo units [28]. We show that the use of DO13 as a building block of micellar aggregates allowed us to manipulate the developed morphology. We analyzed the effect of the change in the micellar morphology over the photoinduced birefringence. The effect of confining DO13 molecules into micellar nanodomains on optical properties was studied.

## 2. Experimental section

### 2.1. Materials

Commercial symmetric diblock copolymer poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP) ( $M_{nPS} = 22\,000$ ,  $M_{nP4VP} = 22\,000$ ,  $M_w/M_n = 1.15$ ) was purchased from Polymer Source and used without further purification. The chromophore selected was a push-pull diazo dye, 4-[4-(phenylazo)-1-naphthylazo]phenol (Disperse Orange 13, DO13, Aldrich). Their chemical structures are shown in figure 1. Poly-4-vinylpyridine (P4VP,  $M_n = 19\,000$ ,  $PDI = 1.15$ , Polymer Source) was used as model compound to probe the H-bond formation with the phenol group of DO13.

### 2.2. Sample preparation

Supramolecular complexes PS-*b*-P4VP(DO13) $_r$  consist of mixtures of azocompound DO13 and PS-*b*-P4VP. In the

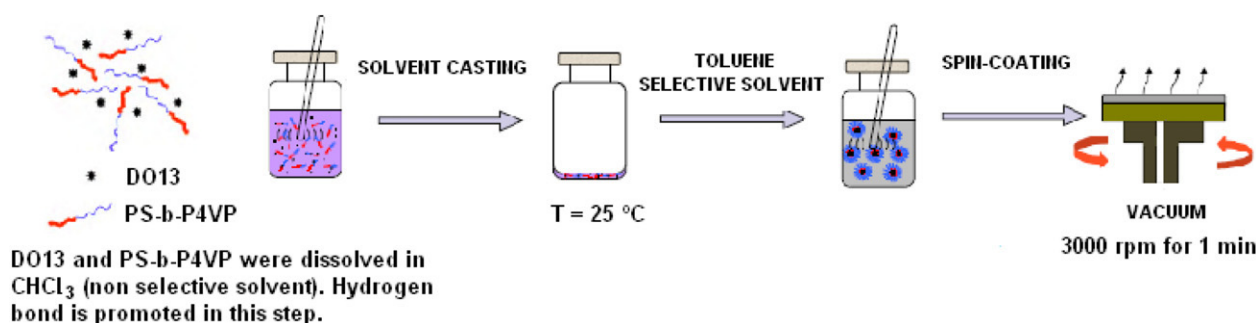


Figure 2. Preparation scheme of the micellar complexes.

Table 1. DO13 wt% as a function of degree of complexation ' $r$ ' in PS-*b*-P4VP(DO13) $r$  complexes.

$r$	DO13 wt%
0.1	14
0.2	25
0.4	40

complexes' code,  $r$  denotes the degree of complexation or, which is also, the number of DO13 molecules per vinylpyridine repeating unit.

PS-*b*-P4VP(DO13) $r$  micellar solutions with different compositions (see table 1) were obtained following a two-step procedure, see figure 2. First, PS-*b*-P4VP and DO13 were dissolved in chloroform. A slight heating (no more than 50 °C) of the solutions was required to ensure complete dissolution of both components. Once completely dissolved, the solution was kept under stirring at room temperature for 24 h, to favor H-bond formation. Second, the chloroform was totally evaporated and the right amount of toluene was added to the residue to attain 0.1 or 3 wt% solutions. Sonication for 30 min followed by stirring for 2 h were necessary to achieve complete dissolution of the residue. Micelles with P4VP core containing the azo dye and PS corona were developed, since toluene is a selective solvent for PS. It should be mentioned that since toluene is not a solvent for DO13, if some DO13 molecules are not attached to the core of the micelles, an orange precipitate should be observed. This was not the case, at least in the range of degree of complexation explored ( $r \leq 0.4$ ).

Thin films of all the cited solutions were prepared by spin-coating on to cleaned glass substrates without any annealing treatment. The spinning program was 3000 rpm for 1 min. Glass substrates were cleaned with acetone, followed by sonication with isopropanol for 30 min, and finally dried under a stream of nitrogen gas. The films were dried in vacuum for 24 h to remove residual solvent.

### 2.3. Characterization

An FT-IR Nicolet 6700 Thermo Scientific device was employed to obtain infrared (IR) spectra in the mid-IR range (400–4000 cm<sup>-1</sup>). The spectra were obtained from polymeric films obtained by casting the complex solutions onto NaCl cells.

The morphology of the polymeric films was characterized by atomic force microscopy (AFM, Agilent Technologies, 5500 scanning probe microscope) imaging operating in tapping mode using a scan rate of 1 line s<sup>-1</sup>.

Differential scanning calorimetry (DSC) was performed using a Pyris 1 device (Perkin Elmer). Glass transition temperature ( $T_g$ ) was measured on the onset of thermograms obtained from second scans performed at 20 °C min<sup>-1</sup>. The samples were prepared from the micellar solutions added drop by drop onto a glass substrate. After evaporating the solvent, 5–10 mg of the sample was taken and encapsulated in an aluminum pan.

UV–visible spectra of DO13 in toluene and PS-*b*-P4VP (DO13) $r$  complexes on thin films were recorded on an Agilent 8453 UV–visible spectrophotometer.

Photo-orientation experiments were carried out at room temperature and under ambient conditions. The optical configuration for the measurement of photoinduced birefringence was identical to that previously reported [29]. Photoinduced birefringence of the resulting films was measured by placing the sample between two crossed linear polarizers. A semiconductor laser at 488 nm was used as the writing beam to induce optical anisotropy in the polymeric film, and a semiconductor laser at 635 nm was used as the reading beam to measure the power that was transmitted through this optical setup. To achieve maximum signal, the polarization vector of the writing beam was set to 45° with respect to the polarization vector of the reading beam. All the films were irradiated with 6 mW of the writing laser in a 0.785 mm<sup>2</sup> spot without observing photobleaching of the films.

The induced birefringence was determined by measuring the probe beam transmission ( $T = I/I_0$ ) according to

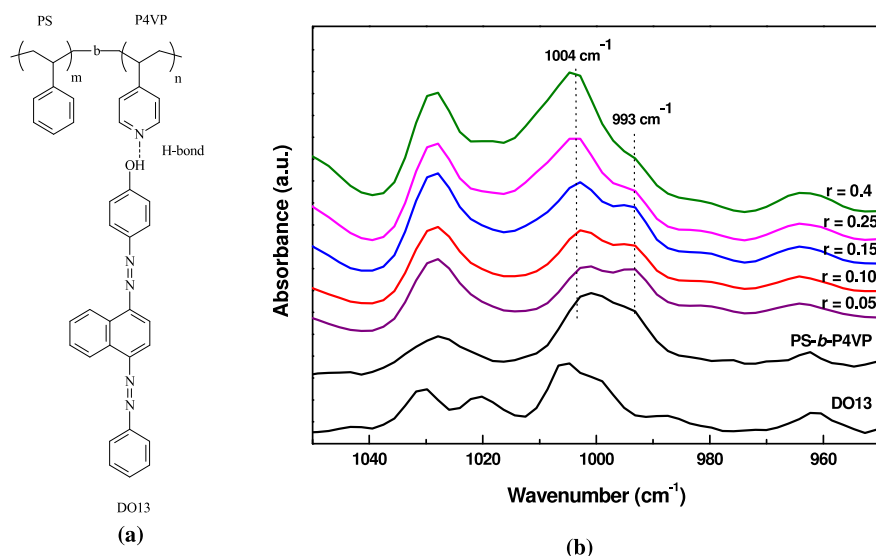
$$\Delta n = (\lambda/\pi d) \sin^{-1}(I/I_0)^{1/2} \quad (1)$$

where  $\lambda$  is the wavelength of the reading beam,  $d$  is the film thickness,  $I$  is the intensity after the second polarizer, and  $I_0$  is the transmitted intensity between parallel polarizers, in the absence of anisotropy.

Film thickness for  $\Delta n$  measurements was calculated from topographic AFM images of scratched films, taking into account the difference in height between a flat area of the sample and the surface of the clean glass slide.

## 3. Results and discussion

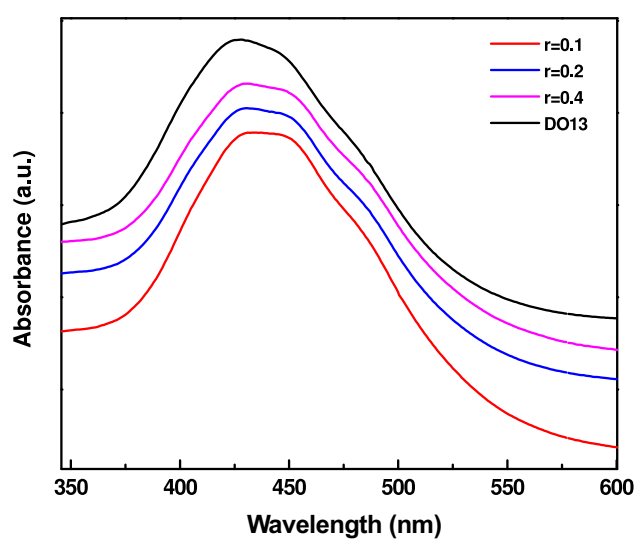
The pyridine groups are hydrogen bonding acceptors that form strong hydrogen bonds with carboxylic acid or phenol groups.



**Figure 3.** (a) Chemical structure of the DBC-based supramolecule, PS-*b*-P4VP(DO13)*r*. (b) Infrared absorption spectra of PS-*b*-P4VP(DO13)*r*, PS-*b*-P4VP and DO13 (at wavenumber region 1050–950  $\text{cm}^{-1}$ ) for different degrees of complexation *r*, at 25 °C. Curves are shifted in the vertical direction for clarity.

It was reported that the P4VP block of PS-*b*-P4VP could be physically attached to phenol groups due to their H-bonding capacity [11, 12, 22, 30–33]. To evaluate the feasibility of this physical union in our system (PS-*b*-P4VP(DO13)*r*), we started using P4VP homopolymer as a model compound. We prepared P4VP(DO13)*r* supramolecule using different degrees of complexation '*r*' and confirmed by FT-IR the development of the H-bond interaction up to equimolar complexation ( $r = 1$ ), see supporting information (available at [stacks.iop.org/Nano/25/065601/mmedia](http://stacks.iop.org/Nano/25/065601/mmedia)). In the case of the supramolecule based on the DBC, which chemical structure is shown in figure 3(a), the formation of the complex was also corroborated. Figure 3(b) shows FT-IR spectra obtained for different values of *r* and those obtained for DO13 and PS-*b*-P4VP as a reference. Pure P4VP has a symmetric ring stretching mode at 993  $\text{cm}^{-1}$  [22, 32, 33]. When complexed with DO13, a new band arises at 1004  $\text{cm}^{-1}$ , which can be attributed to hydrogen bonding between the pyridine and phenol moieties of the chromophore. Note that the relative intensity of the 1004  $\text{cm}^{-1}$  band increases systematically with respect to the 993  $\text{cm}^{-1}$  band as the chromophore content is increased. FT-IR studies verified the formation of hydrogen bonding interactions between 4-vinylpyridine repeating units of the DBC and the azo moieties in the range of degree of complexation '*r*' studied.

Micellar solutions based on PS-*b*-P4VP(DO13)*r* supramolecule were prepared using toluene since it is a selective solvent for PS. Consequently, PS-*b*-P4VP(DO13)*r* comb-coil copolymer spontaneously self-associates into micelles with a soluble PS corona and an insoluble P4VP(DO13)*r* core [25, 26, 34, 35, 20, 36]. These micelles were characterized in terms of UV-vis absorption after being deposited onto glass wafers by spin-coating. The spectra of the films of PS-*b*-P4VP(DO13)*r* containing different concentrations of DO13 ( $r = 0.1$ – $0.4$ ) are presented in figure 4. As a

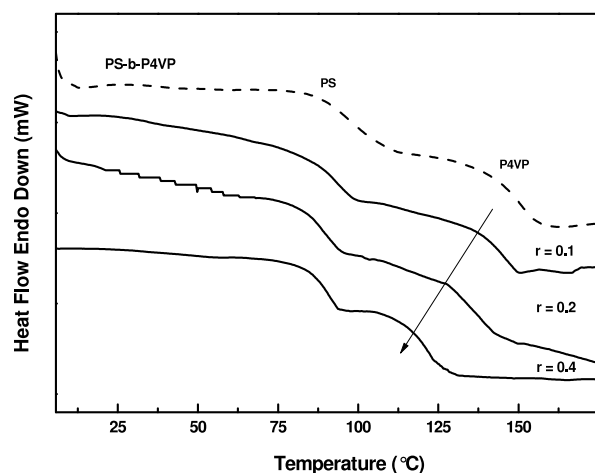


**Figure 4.** UV-visible spectra of PS-*b*-P4VP(DO13)*r* micelles and DO13. Curves are shifted in the vertical direction for clarity.

comparison, the DO13 spectrum in chloroform was added. The main absorption band of the complexes, exhibiting a maximum at 440 nm, presented a red shift with respect to the spectrum of pure DO13 for high *r* samples, probably due to a chromophore–chromophore interaction when DO13 load increases, as it was observed for other supramolecular systems [12].

The micelles were subjected to DSC thermal analysis in order to verify the selective incorporation of the azo moieties into the P4VP block of PS-*b*-P4VP. In view of this, the micellar solutions were dried and placed onto DSC pans and thermograms were obtained from subsequent second scans, see figure 5. PS-*b*-P4VP is an amorphous material with  $T_g$ s at 84 and 135 °C. The lowest  $T_g$  corresponds to the PS block while the highest is assigned to the P4VP block. The incorporation



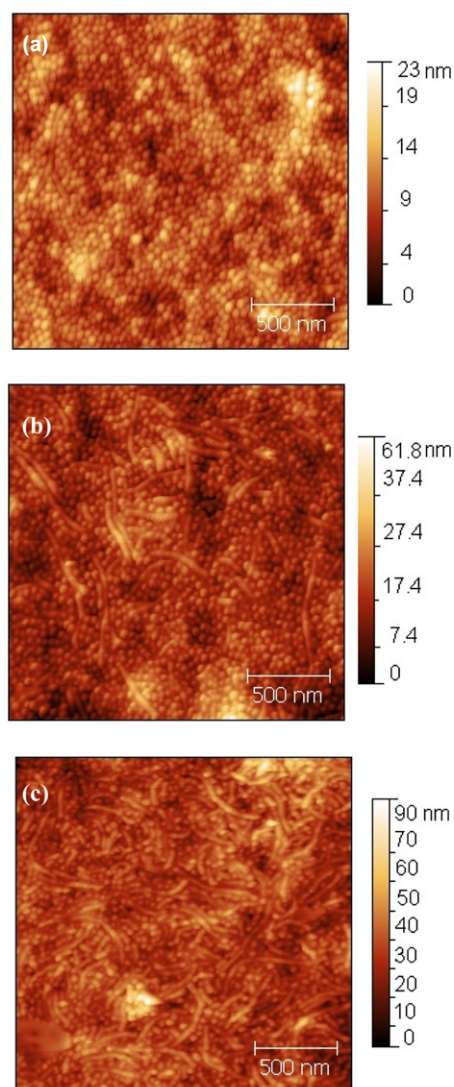


**Figure 5.** DSC thermograms of PS-*b*-P4VP(DO13)*r* micelles and the pure PS-*b*-P4VP. Curves are shifted in the vertical direction for clarity.

of DO13 into the neat DBC produces a drop in the  $T_g$  of the P4VP block which can be attributed to a plasticization effect of the pendant azo moieties hydrogen bonded to the polymer.  $T_g$  decreases systematically as the chromophore content is increased. Instead, the  $T_g$  of the PS block remains unaffected for all the concentrations, indicating that no DO13 is dissolved in the PS phase. Full complexation of the added DO13 with P4VP units indicated the successful selective incorporation of the chromophore into the P4VP core. No other thermal transitions were evidenced in DSC scans.

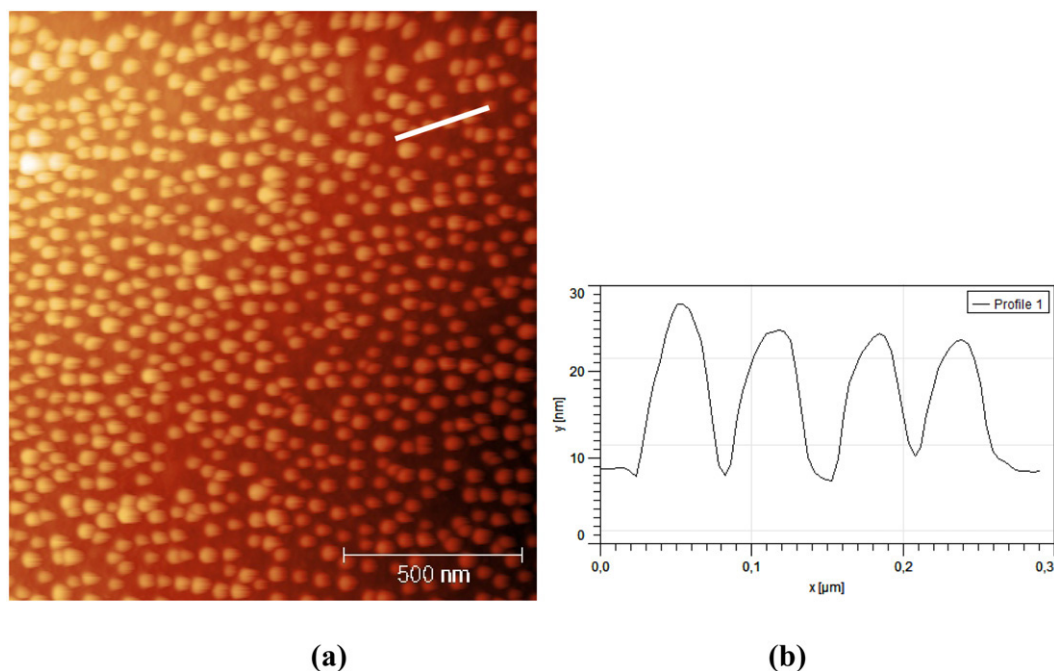
Micellar solutions with different degrees of complexation were prepared at a concentration of 3 wt% in toluene. In order to evaluate the effect of the azo content on the micellar structure developed, these solutions were spin-coated onto glass substrates and the resulting thin films, without any annealing treatment, were analyzed by AFM. In figure 6 we can appreciate three AFM images corresponding to multi-layered thin films of the developed micelles. In figure 6(a), lowest *r*, mostly spherical micelles can be seen (very few cylinders appeared). As *r* increases, figures 6(b) and (c), so does the quantity of cylindrical micelles. Sphere to cylinder transition seems to be promoted by the presence of the azo dye. With increasing DO13 concentration, the micelle cores fused to make cylindrical micelles due to the combined effect of a change in the interfacial tension between the core and the solvent (enthalpic contribution), and stretching caused by the presence of the hydrogen bonded chromophore inside the core (entropic contribution) [37]. The resulting transition from spheres to cylinders might be a way to release the excess in free energy caused by such changes.

Figure 7 shows a thin film (single layer) of spherical micelles obtained by spin-coating a 0.1 wt% solution of PS-*b*-P4VP(DO13)<sub>0.4</sub>. In this case a single-layered film of micelles was obtained without multi-layered structures in accordance with the dilution used. In fact, the bare substrate is sometimes visible in the image, since near 0.5 wt% is necessary for the complete coverage of the substrate [34]. These micelles preserve the composition of the previous ones corresponding to figure 6(c), but were prepared in a



**Figure 6.** AFM images of PS-*b*-P4VP(DO13)*r* micellar aggregates from 3 wt% solution: (a) *r* = 0.1, (b) *r* = 0.2, (c) *r* = 0.4.

more diluted proportion (0.1 wt%). As a result, a completely different scenario consisting of purely spherical micelles was found. It demonstrated the strong effect of the polymer concentration in the solution. Therefore, the formation of cylindrical micelles should be attributed to two factors: the degree of complexation (as it was previously explained), and the polymer concentration in the solution. The last one could be interpreted in terms of the aggregation number of the micelles, defined as the average number of polymer chains in an aggregate. The aggregation number of the micelles, and therefore the micelle core diameter, increases as a function of the polymer concentration in the solution [37]. When polymer concentration increases, so does the size of the core, and the micelles change their morphology from spheres to rods to reduce the entropic penalty associated with the increase in the degree of stretching of the P4VP chains. The increase in the polymer concentration has a morphogenic effect on the aggregates, similar to that of increasing azo loading. It should be pointed out that only spherical micelles were obtained by Park *et al* [35] in solutions of symmetric PS-*b*-P4VP in



**Figure 7.** (a) AFM image of PS-*b*-P4VP(DO13)<sub>0.4</sub> micellar aggregates from 0.1 wt% solution. (b) Height profile for the micellar aggregates of the AFM micrograph marked with the white line.

toluene, when the solution concentration was changed from 1 to 16 wt%.

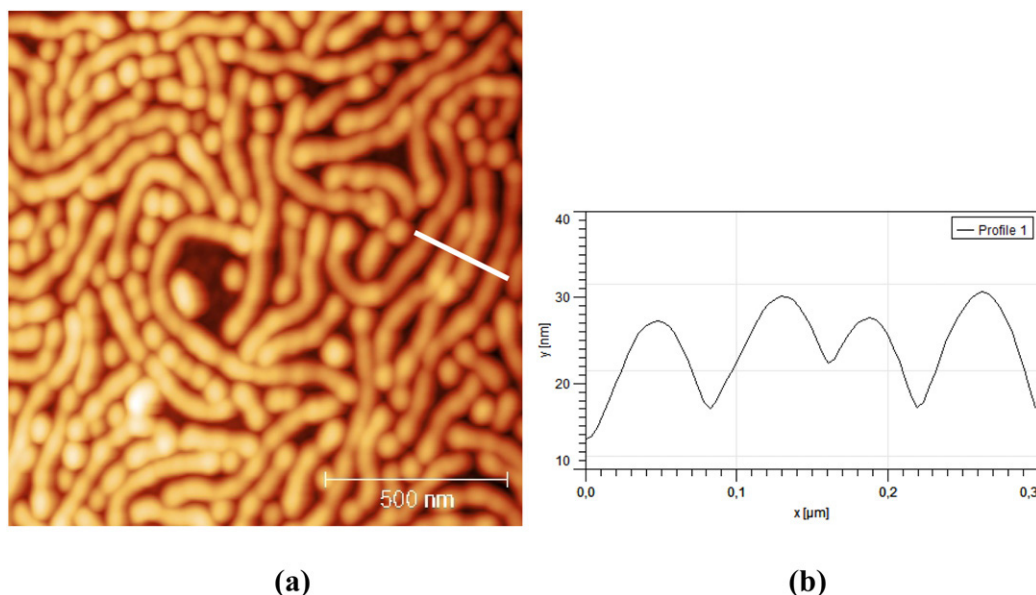
Reversibility between the different morphologies could be analyzed by diluting a more concentrated solution of the polymer aggregates to different concentrations [37]. If the system is thermodynamically controlled, a reversion in the morphology of the aggregates from that of a concentrated solution to that corresponding to a diluted solution is expected. Accordingly, to test the reversibility of our developed solutions containing cylindrical micelles, we diluted the pre-existent micellar solution corresponding to figure 6(c) (mainly cylindrical) up to 0.1 wt% by adding toluene. As the AFM image of figure 8 shows, it was found that the same aggregates that were prepared directly from a dilute solution, exclusively sphericals, can not be obtained by dilution of a more concentrated solution with a different morphology. As can be seen, mainly elongated micelles deposited onto the substrate were found. These micelles displayed a larger average diameter than those prepared from the diluted solution, as can be estimated from comparing the AFM profiles of figures 7 and 8. It is shown that the structures of aggregates are dependent on the procedure of preparation and not on composition, indicating that the system is not under thermodynamic control; on the contrary, it is largely influenced by kinetics. The kinetics mainly depends on the hydrodynamic interactions among the aggregates and the chain mobility in the core. This irreversibility leaves proof of a kinetically frozen morphology, due to the high incompatibility between the core forming P4VP(DO13) and the strong selective solvent employed (toluene).

Until now we have shown how tunable micellar morphologies are readily accessible from solutions of PS-*b*-P4VP(DO13)<sub>r</sub> in a single solvent, just by either varying the stoichiometry between DO13 molecules and DBC or changing

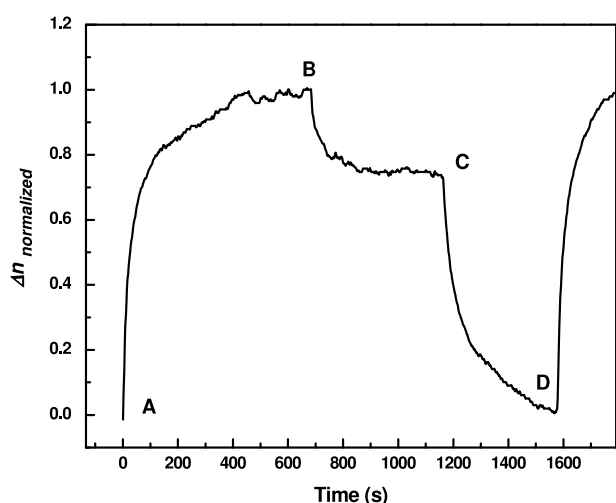
solvent concentration. These micelles could be used to produce azo-containing thin films in which the azo moiety is confined to nanodomains without using any annealing treatment. These films are very interesting due to their potential applications in photonics, since azopolymers are being recognized as promising materials for optical data storage applications [38, 39]. Consequently, we studied the optical behavior of thin films (approximately 40 nm) of micelles of PS-*b*-PVP(DO13)<sub>r</sub> in terms of the optical anisotropy ( $\Delta n$ ) and the remnant birefringence (RB). Desirable characteristics for optical storage systems are short writing and reading times, reversibility after many cycles of writing, high birefringence level and stability of the remnant birefringence [40], and they must be evaluated for this kind of material. As a reference, we compared the results with those of the P4VP(DO13)<sub>r</sub> system, in order to evaluate the existence of any effect of the confinement of azo dyes into nanodomains and/or of the spherical/cylindrical structure when compared to a homogeneous structure (P4VP(DO13)<sub>r</sub>).

An extra advantage of our system is that DO13 bears two isomerizable azobenzene units. The polymeric systems modified with bisazobenzenes are known to give rise to higher and more stable photoinduced anisotropy than the corresponding azobenzene polymers functionalized with monoazo units [28].

A typical sequence of events for a thin film of the PS-*b*-P4VP(DO13)<sub>0.2</sub> micellar system is presented in figure 9. At the beginning of the experiment, no light is transmitted through the analyzer because the azo compound is randomly oriented. The linearly polarized writing laser beam (semiconductor laser, 488 nm) is turned on (A), and the photoinduced birefringence approaches the saturation level. This is a consequence of *trans-cis-trans* photoisomerizations that lead to the orientation of some *trans* molecules perpendicular to the polarization vector of the writing beam. When the excitation light is turned off



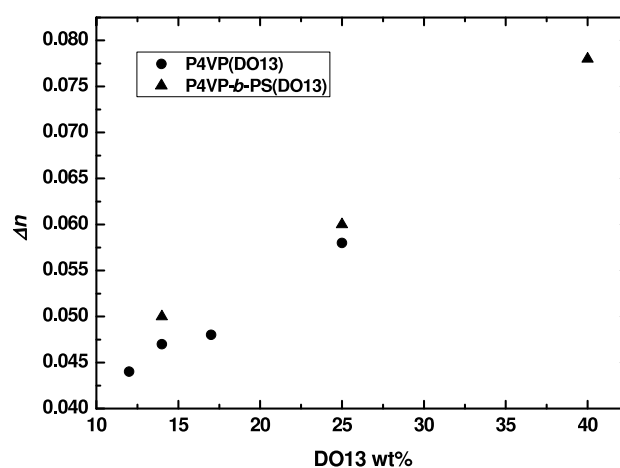
**Figure 8.** (a) AFM image of PS-*b*-P4VP(DO13)<sub>0.4</sub> micellar aggregates from 0.1 wt% solution (dilution of 3 wt% solution). (b) Height profile for the micellar aggregates of the AFM micrograph marked with the white line.



**Figure 9.** Writing, relaxing and erasing sequence of a thin film of PS-*b*-P4VP(DO13)<sub>0.2</sub>: A, writing beam is turned on; B, writing beam is turned off; C, erasing beam is turned on; D, writing beam is turned on again at the same spot.

(B), the signal decreases to a relaxed level called remnant birefringence (RB), due to the thermal reorientation of some azobenzene molecules. There, the rate of change of anisotropy is very small. To remove the remaining birefringence, circularly polarized light is turned on at point C, where the film returns to the isotropic state. At point D the writing beam is turned on again, to start a new writing/erasing cycle, which shows that the photoinduced birefringence is a completely reversible process.

Figure 10 shows the dependence of the optical anisotropy value ( $\Delta n$ ) upon DO13 content for the different films. Optical properties are plotted against DO13 wt% because it allows a better visualization of the results and, besides this, makes the comparison with the homologous homogeneous systems



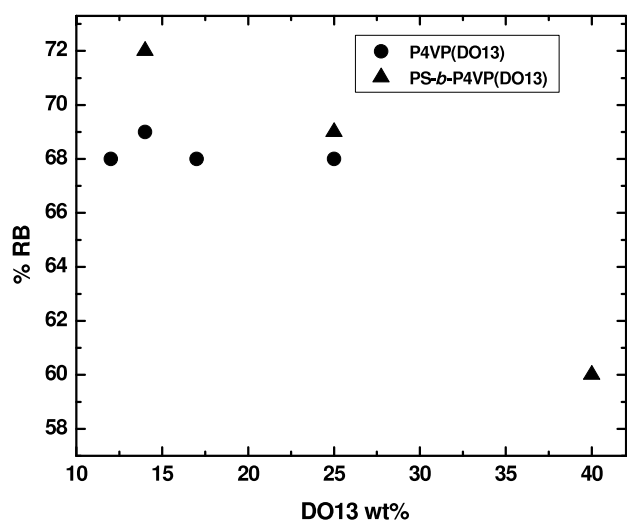
**Figure 10.** Optical anisotropy value ( $\Delta n$ ) as a function of DO13 content.

easier. As guidance to facilitate comparison with previous morphological characterization, see table 1.

The high values of ( $\Delta n$ ) found in all the cases corroborated that hydrogen bonding provides an ideal tool to enhance the optical performance of the material, as was already stated by other research groups [12, 13, 27]. The graph shows an upward trend in the values of birefringence with increasing the amount of DO13, reaching a value of approximately 0.08 for 40 wt% DO13 ( $r = 0.4$ ). The figure also shows that the maximum birefringence values reached for the micellar complexes are higher than those obtained for the homopolymer P4VP, which may be ascribed to the confinement of azobenzene inside the micelles.

Moreover, it is interesting to analyze whether noncovalent interactions can reduce the mobility of the molecules of azobenzene and consequently improve the temporal stability of birefringence. Therefore, we studied the relaxation





**Figure 11.** Remnant birefringence percentage (% RB) as a function of DO13 content.

of the photoinduced birefringence, RB, when the writing laser is removed, figure 11. The micellar systems show an RB slightly higher than the homogeneous P4VP(DO13)*r* system for low chromophore concentration ( $r < 0.2$ ) but it decreases with respect to P4VP(DO13)*r* at higher concentrations ( $r = 0.4$ ). This result could be an effect of the morphology on the optical response, taking into account that the increase of DO13 loading changes the morphology from spheres to cylinders. The reduction of RB could arise from the higher chromophore–chromophore interaction when they are accommodated in a cylinder compared to a sphere structure. In a cylindrical conformation, the interaction among azo molecules is favored leading to some extent of aggregation that, even at a moderate level, could be detrimental to the optical response of the system [41–43]. Considering that complete complexation up to equimolar proportion is achievable according to the results obtained for the homologous homogeneous system (see supporting information, available at [stacks.iop.org/Nano/25/065601/mmedia](http://stacks.iop.org/Nano/25/065601/mmedia)), these findings are novel and pave the way for a future work in which we will analyze how micellar morphology in the film influences the photoresponsive behavior of the material.

#### 4. Conclusions

In this work, we have encapsulated a phenol-functionalized chromophore, DO13, within PS-*b*-P4VP micelles in toluene, by means of H-bond interactions developed between DO13 molecules and pyridine groups of P4VP block. We show how, using a single solvent, either spherical or cylindrical micelles with P4VP(DO13) core and PS corona can be obtained by changing the degree of complexation or solvent concentration. This allows us to conclude that the chain extension and composition of the P4VP micelle core in the presence of the chromophore may be responsible for the structural changes in the micelles. This modification in the micellar structure can be advantageous for the fabrication of porous templates or gratings.

In addition, a preliminary study of the optical properties of micellar thin films has been developed and compared with those of DO13 complexed with P4VP. The optical anisotropy ( $\Delta n$ ) increases with respect to the analogous homogeneous P4VP(DO13)*r* system when the chromophore is located inside the nanodomains formed by the core of micelles. The protective micelle environment enhances the optical properties of the embedded chromophores. Moreover, this investigation shows very interesting new results relating a change in optical properties to the film morphology (spheres to cylinders), which are the subject of our present work.

#### Acknowledgments

The financial support of the University of Mar del Plata, the National Research Council (CONICET) and the National Agency for the Promotion of Science and Technology (ANPCyT), is gratefully acknowledged.

#### References

- [1] Rau H 2002 *Photoreactive Organic Thin Films* ed Z Sekkat and W Knoll (San Diego, CA: Academic) chapter 1
- [2] Förster S and Antonietti M 1998 *Adv. Mater.* **10** 195
- [3] Yu Y and Eisenberg A 1997 *J. Am. Chem. Soc.* **119** 8383
- [4] Hillmyer M A 2007 *Science* **317** 604
- [5] Cui H, Chen Z, Zhong S, Wooley K L and Pochan D J 2007 *Science* **317** 647
- [6] Wang H, Patil A J, Liu K, Petrov S, Mann S, Winnik M A and Manners I 2009 *Adv. Mater.* **21** 1805
- [7] Christian D A, Tian A, Ellenbroek W G, Levental I, Rajagopal K, Janmey P A, Liu A J, Baumgart T and Discher D E 2009 *Nature Mater.* **8** 843
- [8] Hollamby M J, Tabor R, Mutch K J, Trickett K, Eastoe J, Heenan R K and Grillo I 2008 *Langmuir* **24** 12235
- [9] Govorun E N, Ushakova A S and Khokhlov A R 2010 *Eur. Phys. J. E* **32** 229
- [10] Letellier P, Mayaffre A and Turmine M 2008 *J. Colloid Interface Sci.* **321** 195
- [11] Priimagi A, Cattaneo S, Ras R, Valkama S, Ikkala O and Kauranen M 2005 *Chem. Mater.* **17** 5798
- [12] Priimagi A, Vapaavuori J, Rodríguez F J, Faul C F J, Heino M T, Ikkala O, Kauranen M and Kaivola M 2008 *Chem. Mater.* **20** 6358
- [13] Vapaavuori J, Priimagi A and Kaivola M 2010 *J. Mater. Chem.* **20** 5260
- [14] Valkama S, Ruotsalainen T, Nykanen A, Laiho A, Kosonen H, ten Brinke G, Ikkala O and Ruokolainen J 2006 *Macromolecules* **39** 9327
- [15] Osuji C O, Chao C Y, Ober C K and Thomas E L 2006 *Macromolecules* **39** 3114
- [16] Acharya H, Sung J, Sohn B-H, Kim D H, Tamada K and Park Ch 2009 *Chem. Mater.* **21** 4248
- [17] Pan D, Fu Q and Lu J 2012 *Nanotechnology* **23** 305302
- [18] Sohn B H and Seo B H 2001 *Chem. Mater.* **13** 1752
- [19] Koh H-D, Kang N-G and Lee J-S 2007 *Langmuir* **23** 11425
- [20] Cho H, Park H, Park S, Choi H, Huang H and Chang T 2011 *J. Colloid Interface Sci.* **356** 1
- [21] Li W, Liu S, Deng R and Zhu J 2011 *Angew. Chem. Edn* **50** 5865
- [22] Tung S-H, Kalarickal N C, Mays J W and Xu T 2008 *Macromolecules* **41** 6453
- [23] Kao J, Tingsanchali J and Xu T 2011 *Macromolecules* **44** 4392

- [24] Huang W-H, Chen P-Y and Tung S-H 2012 *Macromolecules* **45** 1562
- [25] Rainò G, Stoferle T, Park C, Kim H-C, Chin I-J, Miller R D and Mahrt R F 2010 *Adv. Mater.* **22** 3681
- [26] Ali N and Park S-Y 2009 *Langmuir* **25** 13426
- [27] del Barrio J, Blasco E, Oriol L, Alcalá R and Sánchez-Somolinos C 2013 *J. Polym. Sci. A* **51** 1716
- [28] Meng X, Natansohn A and Rochon P 1997 *Polymer* **38** 2677
- [29] Sáiz L M, Orofino A B, Ruzzo M M, Arenas G, Oyanguren P A and Galante M J 2011 *Polym. Int.* **60** 1053
- [30] Ikkala O, Ruokolainen J, Mäkinen R, Torkkeli M, Serimaa R and ten Brinke G 1999 *Synth. Met.* **102** 1498
- [31] Ikkala O and ten Brinke G 2002 *Science* **295** 2407
- [32] Ruokolainen J, Saariaho M, Ikkala O, ten Brinke G, Thomas E L, Torkkeli M and Serimaa R 1999 *Macromolecules* **32** 1152
- [33] Ruokolainen J, ten Brinke G and Ikkala O 1999 *Adv. Mater.* **11** 777
- [34] Yoo S, Yun S Y, Kim H K and Sohn B-H 2010 *Macromol. Rapid Commun.* **31** 645
- [35] Park S-Y, Sul W-H and Chang Y-J 2007 *Macromolecules* **40** 3757
- [36] Chua K S, Koh A P and Lam Y M 2010 *J. Colloid Interface Sci.* **351** 69
- [37] Zhang L and Eisenberg A 1999 *Macromolecules* **32** 2239
- [38] Natansohn A and Rochon P 1999 *Adv. Mater.* **11** 1387
- [39] Natansohn A and Rochon P 2002 *Chem. Rev.* **102** 4139
- [40] Oliveira O N Jr, dos Santos D S, Balogh D T, Zucolotto V and Mendonça C R 2005 *Adv. Colloid Interface Sci.* **116** 179
- [41] Barto R R, Frank C W, Bedworth P V, Taylor R E, Anderson W W, Ermer S, Yen A K-Y, Luo J D, Ma H, Tang H-Z, Lee M and Ren A S 2006 *Macromolecules* **39** 7566
- [42] Lagugne-Labarthe F, Buffeteau T and Sourisseau C 1998 *J. Phys. Chem. B* **102** 2654
- [43] Zhang Q, Bazuin C G and Barret C J 2008 *Chem. Mater.* **20** 29