Proc. Eurosensors XXV, September 4-7, 2011, Athens, Greece

Photo-detection of solvent polarities using non-invasive coatings in capillaries

Larisa Florea[a], Fernando Benito-Lopez[a*], Alexandre Hennart[a], Dermot Diamond[a]

[a]*CLARITY: The Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland.*

Abstract

Fused silica-capillaries were functionalised with spiropyran-polymer brushes using a spiropyran functionalised norbornyl derivative as the monomer (SP-M). The polymerisation was achieved by surface-initiated ring-opening metathesis polymerisation (Si-ROMP) [1]. We obtained a three dimensional arrangement, covalently attached to the inner wall of the fused-silica capillary, where the spiropyran moiety has the freedom to open and close in response to light (UV, white light). The spiropyran moieties present a very strong dependence on the polarity of the solvent what is expressed by a shift in its main UV-Vis absorption band therefore functionalised capillaries were successfully used to photo-detect solvents of different polarity while passing through the capillary.

Keywords: spiropyran, micro-capillary, ROMP, solvatochromism.

1. Introduction

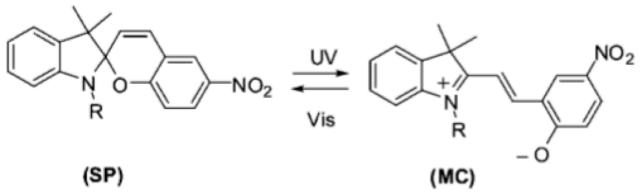
Organic photochromic compounds like spiropyrans are particularly interesting targets for the development of new approaches for sensing. They offer new routes to multifunctional materials that take advantage of their photo-reversible interconversion between two thermodynamically stable states: a spiropyran (SP) form, and a merocyanine (MC) form, which have dramatically different charge, polarity and molecular conformations [2], as shown in Figure 1. This ability to profoundly alter such properties using light has very significant implications for science. In this respect, a significant amount of effort has been devoted to functionalise surfaces with photochromic materials [3]. Functionalisation of the inner wall of a fused silica capillary with this photo-responsive molecule provides a convenient small platform for rapid analysis and detection. Furthermore, continuous flow operation facilitates real-time measurements and consequently fast analysis protocols. Rosario *et al*. coated capillary tubes with a photoresponsive monolayer based on spiropyran, which showed a UV-induced rise (2.8 mm) in water level within a 500 μm channel upon irradiation [4]. Previous work done in our group showed that micro-fluidic channels coated with spiropyran monolayers can be used as photonically controlled self-indicating systems for metal ion accumulation and release [3], based on the metal ion-binding and molecular recognition properties which are only manifested by the MC form.

It is well known that the open-chain merocyanine forms of spiropyrans have been found to beare negatively solvatochromic, meaning that their absorption bands undergo a hypsochromic (blue) shift in solvents of increasing polarity. These changes are caused by intermolecular interactions between the

*Corresponding author. Tel.: + 353 1 700 7603; fax: + 353 1 700 7995.
E-mail address: fernando.lopez@dcu.ie.

solute and solvent that modify the energy gap between the ground and excited states of the absorbing species. The solvatochromism of the open-chain merocyanine forms of spiropyrans has been studied primarily for its potential use as an empirical indicator of solvent polarity [5].

In this context, we are focusing on the development of miniaturised analytical platforms wherein solvent polarity can be externally photo-detected in a completely non-invasive manner, due to the colour dependence of the MC form on the solvent polarity. The coating of fused-silica micro-capillaries with photochromic polymer brushes containing spiropyran moieties was achieved using surface-initiated ring-opening metathesis polymerization (SI-ROMP). This approach offers a transition from a two-dimensional to a three-dimensional arrangement, which enables high surface loadings of the stimuli-responsive polymer and enhances the switching effect compared to conventional films [1].



Scheme 1. Isomeric molecular structure of a spiropyran irradiated with light, spiropyran (left) and merocyanine (right).

2. Experimental

2.1. Materials and instruments

7-Octenyltrichlorosilane (Gelest), and Grubbs Generation-II catalyst (Aldrich) were used as received. Acetone, acetonitrile, dry tetrahydrofuran (THF), dry toluene and dry dichloromethane (CH2Cl2) solvents were purchased from Aldrich and used as received. The norbornyl functionalised spiropyran monomer (SP-M) was produced as described elsewhere [1]. Fused-silica capillaries (100 µm ID, 375 µm OD) were purchased from Polymicro Technologies (Phoenix, AZ, USA). UV–vis spectra for the spiropyran solutions were recorded on a UV–vis–NIR PerkinElmer Lambda 900 spectrometer. The UV irradiation source (BONDwand UV-365 nm) was obtained from the Electrolite Corporation. The optical switching of the spiropyran moiety inside the capillary has been studied using USB 2.0 Fiber Optic Spectrometer – Ocean Optics, Inc, when the light source was a LS-1 tungsten halogen lamp (white light) obtained from Ocean Optics, Inc. The syringe pump used was a PHD 2000 Syringe purchased from Harvard Apparatus. Scanning electron microscopy images were performed on a Carl Zeiss EVOLS 15 system.

2.2. Procedure used to coat fused silica micro-capillaries with spiropyran-based polymer brushes using Si-ROMP.

Prior to functionalisation, the inner surface of fused-silica capillaries was first activated with 7-octenyl trichlorosilane. The inner capillary surface was quickly washed with acetone and water, then flushed with a solution of NaOH 0.2 M for 30 min at a flow rate of 0.25 µl/min using a syringe pump, and then rinsed with deionised water. Next, the capillary was flushed with a solution of HCl 0.2 M for 30 min at a flow rate of 0.25 µl/min, rinsed with water, and with dry toluene. A 0.1 M solution of the silanisation agent (7-octenyl trichlorosilane) 0.1 M in dry toluene was pumped through the capillaries for 90 min at a flow rate of 0.25 µl/min. The capillaries were then washed with acetone, dried under nitrogen stream, and

left at room temperature for 24h. Later, the capillary was filled with a solution of Grubbs Catalyst Second Generation 0.02 M in degassed CH_2Cl_2, closed at both ends and put in a water bath for 1h at 45 °C. After the catalyst-attached capillary was thoroughly washed with degassed CH_2Cl_2. Finally, the capillary was exposed to the spiropyran functionalised monomer, **SP-M** 0.5 M in degassed CH_2Cl_2 at 50°C for 4 h. The polymerisation was quenched by passing ethyl vinyl ether into the capillary. Finally the capillary was thoroughly washed with acetone to remove any physisorbed materials.

3. Results and discussions

3.1. Characterisation of Spiropyran polymer brushes inside the capillary.

SI-ROMP reactions of spiropyran functionalised norbornene monomer were carried out from the walls of the fused-silica capillary as described in the experimental section. Using this technique, polymer brushes with a thickness of about 1µm were obtained, as shown in Figure 2.

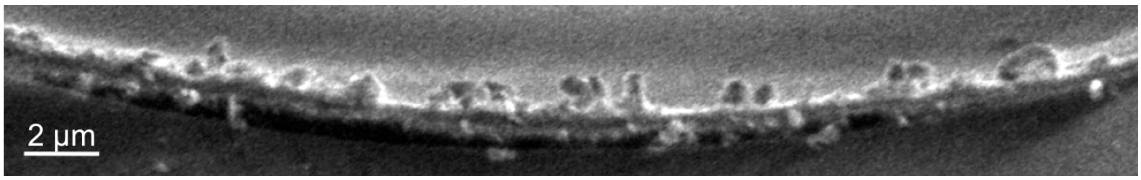


Fig. 2. Scanning electron microscopy image of the inner wall of a fused silica capillary (100 µm inner diameter) after functionalisation with the spiropyran polymer brushes.

3.2. Solvent detection

The colored MC form shows solvatochromism in neat solvents. The stabilization of the MC form in polar solvents leads to a larger activation energy than in nonpolar solvents. When SP-M is irradiated with UV light in Toluene and ACN (Fig. 3 - left), the open form (MC) presents an absorption peak at 609 nm in Toluene and a significant hypsochromic (blue) shift in λ_{max} (568 nm) for ACN, which indicates a significantly more polar micro-environment. When the SP-M functionalised capillary is filled with Toluene, and ACN, respectively, the same type of shift is observed (Fig. 3 - right). This absorption band disappears after irradiation of the solution with white light for 20 seconds because of the switching of the merocyanine molecule back to the closed spiropyran form. The absorption spectra are accompanied by photos of the SP-M monomer solutions in the two solvents, after being exposed to UV and white light and photos of the functionalised capillary when filled with ACN, and Toluene, respectively, after irradiation with UV and white light (Fig 4). The shift of the λ_{max} in the absorption spectra of the polymer brushes compared to that of the monomer solutions is most likely due to local environmental effects related to the immobilization of the spiropyran moiety.

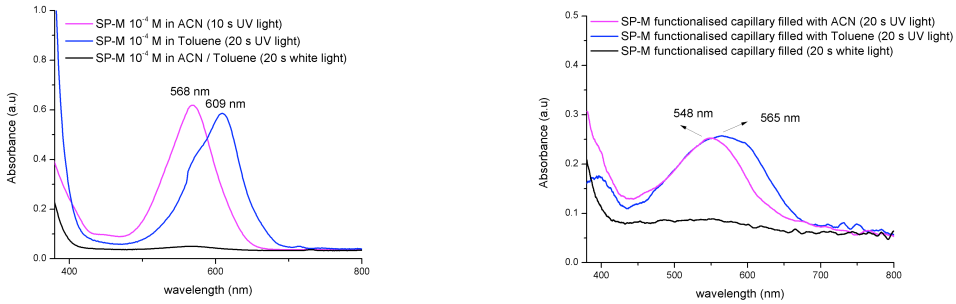


Fig 3. Absorption spectra of the SP-M monomer solution in ACN and Toluene, respectively, after irradiated with UV and white light (left) and absorption spectra of SP-M – based polymer brushes functionalised capillary irradiated with UV and white light in ACN and Toluene, respectively (right).

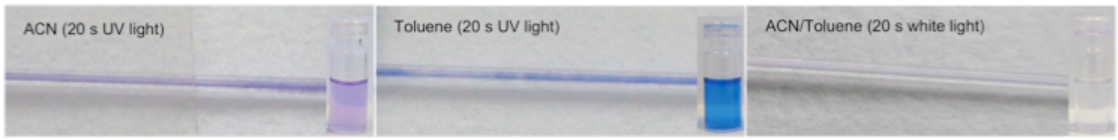


Fig 4. Photos of the SP-M monomer solutions and photos of the functionalised capillary in ACN, and Toluene, respectively, after irradiation with UV and white light.

4. Conclusions

To our knowledge this is the first time spiropyran based polymer brushes were grafted on the inner walls of a micro-capillary. Here, we demonstrate a self-diagnosing miniaturised analytical platform, capable of detecting and reporting variations in the local polarity along the length of the capillary through changes in the capillary colour and shifts in the λ_{max} (*e.g.* using imaging spectroscopy). Furthermore, this sensing behaviour can be switched on/off remotely using light, either along the entire length of the capillary, or at patterned locations using appropriate masks.

5. Acknowledgements

The project has been carried out with the support of the Irish Research Council for Science, Engineering and Technology (IRCSET) - Embark Initiative and Science Foundation Ireland under grant 07/CE/I1147.

References

[1] Samanta S, Locklin J, Formation of photochromic spiropyran polymer brushes via surface-initiated, ring-opening metathesis polymerization: reversible photocontrol of wetting behavior and solvent dependent morphology changes. *Langmui*r 2008;24:58–65.

[2] Minkin VI, Photo-, thermo-, solvato-, and electrochromic spiroheterocyclic compounds. *Chemical Reviews* 2004;**104**:2751–6.

[3] Benito-Lopez F, Scarmagnani S, Walsh Z, Paull P, Macka M, Diamond D, Spiropyran modified micro-fluidic chip channels as photonically controlled self-indicating system for metal ion accumulation and release. *Sensors and Actuators B* 2009;**140**:295–303

[4] Rosario R, Gust D, Hayes M, Jahnke F, Springer J, Garcia AA, Photon-modulated wettability changes on spiropyran-coated surfaces. *Langmuir* 2002;**18**:8062–8069.

[5] Rosario R, Gust D, Hayes M, Springer J, Garcia AA, Solvatochromic study of the microenvironment of surface-bound spiropyrans. *Langmuir* 2003;**19**:8801–8806.