Reversible photochromic polynorbornenes bearing spiropyran side groups for layer-by-layer coatings

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Outline

Background

Photochromic polynorbornenes bearing spiropyran side groups

- Spiropyran norbornene monomer
- Spiropyran polynorbornene
- Characterisation
- LbL assembly
- Photo-induced dissassembly
- Photo-responsive drug delivery capsules

Conclusions
Spiropyrans

A : Spiropyran SP (closed, colorless)  B : Merocyanine MC (open, colored)
Spiropyran-Based Polymers

Most protocols for the incorporation of SP units into polymer matrices generally involve polymerisation of derivatised SP monomers or copolymerisation of these species with compatible monomeric units, where the SP moiety can be introduced as side chain or as a part of the main polymer chain.

Other methods include non-covalent doping/entrapment of SP derivatives within various polymer matrices or functionalisation of pre-formed polymers with SP pendant groups.

A number of examples of SP-based polymer most often presented in recent literature are described in Table 1 and comprise a series of homo- and co-polymers obtained through various polymerisation techniques: radical polymerisation, atom-transfer radical polymerisation (ATRP), ring-opening metathesis polymerisation (ROMP) and photo-polymerisation, among others. Other types of polymers in which the SP is included as a pendant group post polymerisation or simply used as a dopant are also presented. Table 1 gives an overview of polymers containing SP where the emphasis is on their structure. SP polymeric systems can be used for a variety of applications, showing that by combining the key advantages of the SP moiety with the smart engineering of SP-based polymers, new materials with designed macroscopic properties can be obtained. Various types of SP polymers have been designed in order to acquire photo-control over specific characteristics of the material like permeability towards different analytes, wettability, sensing behaviour, actuation and electrical properties or to visualise mechanical stress. The following sections will discuss specific SP polymeric systems based on their photo-modulated properties.

3. Photo-Modulated Wettability

The wettability of surfaces depends on both, the surface chemistry and the surface morphology, in particular, on the micro-structures of the surface. Having the possibility to...

Spiropyrans

Photo-responsive polymers

Spiropyran norbornene monomer

SP

\[ \text{Spiropyran norbornene monomer} \]

\[ \begin{align*}
\text{SP} + \text{COOH} &\rightarrow \text{SP-M} \\
\text{DCC, DMAP} &\rightarrow \text{THF, RT, 24h}
\end{align*} \]

Absorbance [a.u.]

Wavelength (nm)
Spiropyran norbornene monomer
Spiropyran norbornene monomer
Polymerisation of Spiropyran Monomer

Ring-opening metathesis polymerisation

$$m=80,100,300$$
Polymer Characterisation

Absorbance [a.u.]

Wavelength (nm)

% Transmittance

Wavenumber (cm$^{-1}$)

MC

SP

Polymer Characterisation

[Chemical structures and data]
Merocyanine polymers for LbL coatings

LbL coatings
LbL coatings
LbL coatings

A

Absorbance at $\lambda_{\text{max}} = 590$ nm (a.u.)

Number of Bilayers

B

Image of a sample with a gradient from bottom to top.
LbL coatings

- SEM imaging
Photo-induced dissassembly

- Absorbance at 590nm decreases by 60% under white light irradiation
Conclusions

• Synthesised a new polynorbornene spiropyran polymer.
• Characterised spiropyran monomer and polymer.
• Developed new layer-by-layer coatings which disassemble under white light irradiation.
• Development of photo-responsive drug delivery capsules
FO-8:P01 Photo-responsive Soft Actuators based on Spiropyran Functionalised hydrogels
A. Dunne, L. Florea, D. Diamond

FO-8:P09 Stimuli-controlled Movement of Droplets and Polymeric “Vehicles”
W. Francis, L. Florea, D. Diamond
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