Multiresponsive Spiropyran-based Copolymer: Synthesis and characterization

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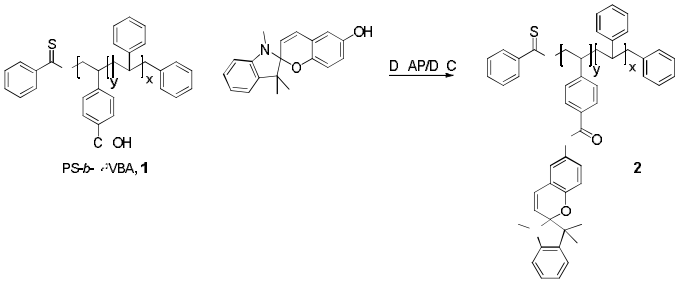
Photochromic copolymers carrying spiropyran side groups have attracted particular attention for potential applications in optical devices, photonic memory and photosensing, as well as, fluorescence imaging.[1] These materials allow overcoming many of the limitations inherent to traditional spiropyran doped polymers, such as, phase separation of the colorant and retardation of the decoloration of the open form.[2] The introduction of light sensitive moieties within responsive polymers has led to the development of sophisticated multiresponsive systems.[3] Block copolymers are important self-assembling systems that can assume a diversity of nanometer-scale morphologies due to the incompatibility and the connectivity constrains between the chemically distinct segments. Therefore, self-assembly of photochromic copolymers in the solid state or in solution allows the development of nanostructured materials. [4]

The aim of this research study is the synthesis of a multiresponsive spiropyran-based copolymer, poly(styrene)-*co*-poly([1´,3´,3´-trimethyl-6-methacryloyloxyspiro(2H-1-benzopyran-2,2´-indoline)]4-vinylbenzoic acid) **2**. The functionalized block copolymer poly(styrene)-*block*-poly(4-vinylbenzoic acid) (PSt-*b*-P4VBA) **1** synthesized by reversible addition fragmentation chain-transfer (RAFT) polymerization was coupled with 1,3,3-trimethyl-6-hydroxyspiro(2H-1-benzopyran-2,2-indoline). The link between the functionalized block copolymer and spiropyran was successfully obtained by Steglich esterification using DMAP/DCC as catalysts (**Scheme 1**).



Scheme 1

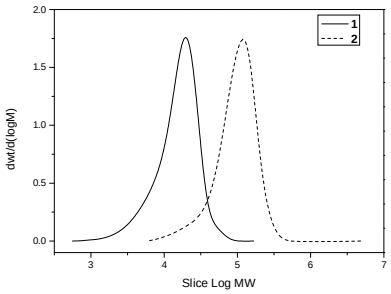


Figure 1

Gel permeation chromatography (GPC) results confirmed the insertion of spiropyran units into the PSt-*b*-P4VBA copolymer (**Figure 1**). Photosensitivity properties of the newly synthesized copolymer **2** are very promising.

[1] Y. Shiraishi, R. Miyamoto, T. Hirai, *Organic Letters* 2009, *11*, 1571-1574.
[2] D. S. Achilleos, M. Vamvakaki, *Macromolecules* 2010, *43*, 7073-7081.
[3] K. Sumaru, M. Kameda, T. Kanamori, T. Shinbo, *Macromolecules* 2004, *37*, 4949-4955.
[4] F. H. Schacher, P. A. Rupar, I. Manners, *Angewandte Chemie International Edition* 2012, *51*, 7898-7921.

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