## SWITCHING FROM RAFT TO ROP: A FACILE ROUTE TO COMPLEX AND SULFUR-FREE MACROMOLECULAR ARCHITECTURES

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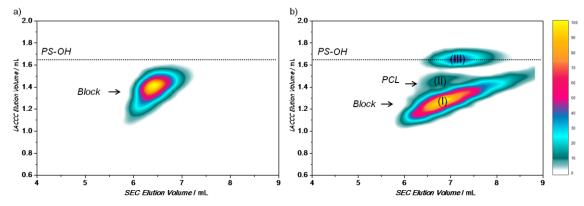
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## ABSTRACT

The provision of efficient avenues for block copolymers synthesis is an important contemporary research theme, as such structures find wide applications in the generation of self-organizing systems, polymer based therapeutics and optoelectronics. The generation of block copolymers has been greatly simplified via the introduction of reversible activation/deactivation radical polymerization processes including the reversible addition fragmentation chain transfer (RAFT) process. A particular interesting area in the field of block copolymer generation is the switching from one polymerization technique to another during the synthetic process. We have recently introduced a method for quantitatively switching RAFT prepared polymers into hydroxyl functional macromolecules that contain no sulfur and merely consist of the backbone monomer repeat units with a terminal OH function.<sup>1</sup> This macroinitiator is employed in the ROP of  $\varepsilon$ -caprolactone ( $\varepsilon$ -CL), producing variable molecular mass, sulfur free narrow polydispersity PS-*b*-PCL block copolymers.<sup>2</sup> The ring opening polymerization (ROP) of  $\varepsilon$ -caprolactone ( $\varepsilon$ -CL) was conducted under organo-catalysis employing 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).



*Figure 1:* 2D plots of a) the pure block copolymer pS-b-pCL and b) a block copolymer pS-b-pCL with homopolymer residues under critical conditions of polystyrene (THF (88.4 wt%) and water (11.6 wt%)). The dotted line represents the peak maximum of the polystyrene-OH under critical conditions.

The obtained block copolymers were thoroughly analyzed via size exclusion chromatography (SEC), NMR as well as liquid adsorption chromatography under critical conditions coupled to size exclusion chromatography (LACCC-SEC, see Figure 1) to evidence the block copolymer structure and the efficiency of the synthetic process. The current contribution demonstrates that the RAFT process can serve as a methodology for the generation of sulfur free block copolymers via an efficient end group switch.

## **References**

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