SYNTHESIS OF FUNCTIONAL BLOCK COPOLYMERS BY CONTROLED RADICAL POLYMERIZATION TECHNIQUES

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There is increasing interest in designing block copolymer with "smart" molecular architectures capable to carry out a variety of functions. Comprising, at least, two chemically different polymer segments, block copolymer combine the properties of the both original polymers, offering the possibility to tailoring the physico-chemical and thermo-mechanical properties to obtain new engineering materials [1].

Controlled radical polymerization (CRP) techniques have been widely used for the preparation of several block polymers with controlled molecular weight, narrow polydispersity and well-defined architecture (e.g. block, gradient and graft copolymers and stars). The most useful CRP techniques include nitroxide-mediated polymerization (NMP) [2], atom transfer radical polymerization (ATRP) [3] and reversible addition fragmentation chain transfer (RAFT) polymerization [4]. The core of CRP process lies on the propagation polymer radicals equilibrium between active and dormant chains through a reversible activation/deactivation states. In CRP, polymerization is mediated by functional monomers, where the leaving and the activating groups of the monomers are retained at the ends of the resulting polymers. This preservation, results in polymers with specific functional end groups, according to RAFT agent selected, which can be submitted to a variety of post-polymerization modifications. The terminated groups presented in polymers after CRP polymerization have a variety of applications, as to click chemistry, functional nanoparticles and biopolymer or to multiblock copolymers [5].

Our research focuses on study of styrene, 9-vinylanthracene, 4-vinylbenzoic acid, 4-vinylaniline, n-vinylcaprolactam, n-vinylcarbazole and phenyl vinyl sulfoxide monomers, respectively. Block copolymers with different conjugations were evaluated and properties determined.

References

- 1. Saif Ullah Khan, M., et al., Synthesis, characterization and morphological studies of some novel siloxane-based block copolymeric materials containing organometallic as well as organic polyesteramides. Journal of Organometallic Chemistry, 2013. **745**–**746**(0): p. 312-328.
- 2. Hawker, C.J., A.W. Bosman, and E. Harth, *New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations*. Chemical Reviews, 2001. **101**(12): p. 3661-3688.
- 3. Matyjaszewski, K., *Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives.* Macromolecules, 2012. **45**(10): p. 4015-4039.
- Keddie, D.J., A guide to the synthesis of block copolymers using reversible-addition fragmentation chain transfer (RAFT) polymerization. Chemical Society Reviews, 2014.
 43(2): p. 496-505.
- 5. Roth, P.J., et al., Versatile ω -end group functionalization of RAFT polymers using functional methane thiosulfonates. Journal of Polymer Science Part A: Polymer Chemistry, 2009. **47**(12): p. 3118-3130.