Combining steric and electrostatic stabilization using hydrophilic macroRAFT agents in an *ab initio* emulsion polymerization of styrene.

Amilton Martins Dos Santos,[1,2] Jordan Pohn,[2,3] Muriel Lansalot,[4] Franck D'Agosto[2]
*muriel.lansalot@ens-lyon.fr
1. Laboratório de Polímeros, Departamento de Engenharia Química, Escola de Engenharia de Lorena - USP, Estrada Municipal do Campinho, s/nº, CP 116, 12.602.810, Lorena (SP), Brasil.
2. Laboratoire de Chimie et Procédés de Polymérisation, C2P2 5265 CNRS/ESCPE, Bât 308 F, 43 Boulevard du 11 Novembre 1918, BP 2077, 69616 Villeurbanne CEDEX, France.
3. Department of Chemical Engineering Queen's University Dupuis Hall 19 Division St.Kingston, Ontario, Canada K7L 3N6.
4. Unité Mixte CNRS/bioMérieux, École Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France.

Poly(ethylene oxide) (PEO)-based molecules have demonstrated their unique potential for latex syntheses and are considered as an important class of surfactants in industry. The efficiency of the stabilization strongly depends on the anchorage of the PEO part on the surface of the latex particles. Various strategies have thus been employed in the literature to introduce PEO segments onto the surface of latex particles via physical adsorption of amphiphilic block copolymers. However, depending on the affinity between the adsorbing block and the particle surface, they may be rapidly desorbed after latex syntheses. To overcome this drawback, PEO segments can be anchored using for instance thiol-ended PEO chains as chain transfer agent-surfactant (transurf)[1]. Thiocarbonyl thio compounds of structure R-SC(=S)-Z are much more efficient chain transfer agents than thiols. Indeed, when Z and R groups are properly chosen, a very fast and reversible transfer can be induced. This feature is at the origin of the powerful RAFT polymerization technique[2]. In this process all the chains carry a thiocarbonyl thio chain end functionality (-SC(=S)-Z) at the end of the polymerization. For polymerization in dispersed media, one may take advantage of the reactivity of this chain end to produce stabilizers via the in situ formation of surface active block copolymers, providing new tools to design latex surfaces[3,4].
This paper focuses on the synthesis of electrosterically stabilized PS latex particles, by combining cationically charged RAFT synthesized polymer chains with PEO-RAFT chains. Protonated form of poly(dimethylaminoethyl methacrylate) (P(DMAEMA/H^+Cl^-)-RAFT), recently synthesized in our group by the RAFT process[5], was first tested as a potential highly hydrophilic precursor of stabilizer in an *ab initio* batch emulsion polymerization of styrene performed under acidic conditions. Then, a hydrophilic PEO-RAFT was synthesized and used in conjunction with P(DMAEMA/H^+Cl^-)-RAFT for the production of double stabilized PS latex. Finally, the double stabilization strategy was further investigated using a PEO-*b*-P(DMAEMA/H^+Cl^-)-RAFT block copolymer, a single molecule capable of providing electrosteric stabilization in one step. Beneficial aspects of the resulting double stabilization were evidenced by comparing the behavior toward pH variations and freeze-thaw cycles of these latexes.

References

(1) Bourgeat-Lami, E.; Guyot, A. *Colloid Polym. Sci.* **1997**, *275*, 716-729.
(2) Chiefari, J.; Chong, Y.K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T.P.T.; Mayadunne, R.T.A.; Meijs, G.F.; Moad, C.L.; Moad, G.; Rizzardo, E.; Thang, S.H. *Macromolecules* **1998**, *31*, 5559-5562.
(3) a) Ferguson, C.J.; Hughes, R.J.; Nguyen, D.; Pham, B.T.T.; Gilbert, R.G.; Serelis, A.K.; Such, C.H.; Hawkett, B.S. *Macromolecules* **2005**, *38*, 2191-2204. b) Ferguson, C.J.; Hughes, R.J.; Pham, B.T.T.; Hawkett, B.S.; Gilbert, R.G.; Serelis, A.K.; Such, C.H. *Macromolecules* **2002**, *35*, 9243-9245.
(4) Manguian, M.; Save, M.; Charleux, B. *Macromol. Rapid Commun.* **2006**, *27*, 399-404.
(5) Sahnoun, M.; Charreyre, M.-T.; Veron, L.; Delair, T.; D'Agosto, F. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 3551-3565.