

Key Steps Toward a New Generation of Controlled Radical Polymerization in Miniemulsion and Emulsion

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Among controlled radical polymerization techniques, iodine transfer polymerization (ITP) based on the use of alkyl iodides as reversible transfer agents has already led to commercial products.¹ Very recently, we published a new controlled radical polymerization method based on the use of molecular iodine I₂ (a cheap and easily available compound) in combination with a conventional radical initiator (ex: 2,2'-azobisisobutyronitrile).² The so-called *Reverse Iodine Transfer Polymerization* (RITP) offers significant advantages over other methods: it does not require the synthesis nor storage of control agents, does not make use of metals, works at moderate temperature, and produces uncolored polymers. On top of this, RITP has been successfully applied to several classes of monomers (ex: acrylates, methacrylates, styrenics, vinylidene halides) in homogeneous homo- and copolymerizations and is economically much more attractive than any other controlled radical polymerization techniques developed so far.³⁻⁶

Controlled radical polymerizations in aqueous emulsion are generally facing many problems related to the instability of the species in the presence of water and the partitioning of the species between the different phases.⁷⁻⁸ Several approaches have been attempted to overcome these problems in NMP, ATRP, and RAFT polymerization in emulsion, mainly using multi-step procedures. We will present in this communication our recent experience on aqueous miniemulsion⁹ and ab initio emulsion RITP of butyl acrylate, styrene, and methyl methacrylate. The careful analysis of the chemistry of iodo-compounds in water media allowed us to elaborate improved RITP procedures, including redox processes, to ensure a facile, flexible and robust controlled polymerization process.¹⁰⁻¹¹ These studies show that it is now possible to reach unprecedented high level of control over molecular weights and good livingness by RITP in aqueous dispersed media. Finally, a totally new generation of RITP in dispersed aqueous media will be presented that is particularly suitable for industrial developments.

References

- (1) David, G.; Boyer, C.; Tonnar, J.; Ameduri, B.; Lacroix-Desmazes, P.; Boutevin, B. *Chem. Rev.* **2006**, *106*, 3936-3962.
- (2) Lacroix-Desmazes, P.; Severac, R.; Boutevin, B. *Macromolecules* **2005**, *38*, 6299-6309.
- (3) Lacroix-Desmazes, P.; Severac, R.; Otazaghine, B.; Boutevin, B. *Polym. Prepr. (ACS, Polym. Div.)* **2003**, *44(2)*, 683-684.
- (4) Lacroix-Desmazes, P.; Severac, R.; Boutevin, B.; Bodart, V.; Kurowsky, V. *WO 03097704*, **2003**, Chem. Abstr. 2003:914240.
- (5) Lacroix-Desmazes, P.; Severac, R.; Boutevin, B.; Bodart, V.; Kurowski, V. *WO 2004094356*, **2004**, Chem. Abstr. 2004:927153.
- (6) Boyer, C.; Lacroix-Desmazes, P.; Robin, J.-J.; Boutevin, B. *Macromolecules* **2006**, *39*, 4044-4053.
- (7) Tonnar, J.; Lacroix-Desmazes, P.; Boutevin, B. *Macromol. Rapid Commun.* **2006**, *27*, 1733-1738.
- (8) Tonnar, J.; Lacroix-Desmazes, P.; Boutevin, B. *ACS Symp. Ser.* **2006**, *944*, 604-619.
- (9) Tonnar, J.; Lacroix-Desmazes, P.; Boutevin, B. *Macromolecules* **2007**, *40*, 186-190.
- (10) Lacroix-Desmazes, P.; Tonnar, J.; Boutevin, B. *Macromol. Symp.* **2007**, *248*, 150-157.
- (11) Tonnar, J.; Lacroix-Desmazes, P.; Boutevin, B. *Macromolecules* **2007**, ASAP.