***Macromolecular engineering of electroactive fluoropolymers***

Vincent LADMIRAL

ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, FRANCE

***Abstract***

Fluoropolymers are an important class of polymers endowed with remarkable properties (ferro- and piezoelectricity).[1] The development of efficient Reversible Deactivation Radical Polymerization (RDRP) techniques for VDF (and TrFE) has not been as fast or intense as that of other vinyl monomers. Until recently, only Iodine Transfer Polymerization was able to afford some degree of control on the polymerization of VDF. This talk will provide a detailed account of the recent advances made in the RDRP of VDF and TrFE using RAFT[2,3] and CMRP[4] techniques. The monomers were homopolymerized in the presence of *O*-ethyl-*S*-(1-methoxycarbonyl)ethyldithiocarbonate and tert-amyl peroxy-2-ethylhexanoate as xanthate chain transfer agent and initiator respectively in dimethyl carbonate at 74 °C. Due to reverse addition these polymerizations lead to two different dormant species: the regularly and inversely terminated PVDF and PTrFE chains. Due to the much lower reactivity of the dormant chains resulting from a head-to-head addition these dormant species accumulate very fast in the reaction medium until they constitute 100% of the xanthate-terminated chains. After this point, the RAFT equilibrium slows down and the control of the polymerization is severely degraded.[5] In addition, both polymerization are severely affected by hydrogen abstraction leading to H-terminated dead-chain. In the case of VDF, a head-to-head addition is always followed by a tail-to-tail addition. In contrast, our NMR study revealed tail-to-head additions (reverse propagation) in the case of TrFE. In spite of the aforementioned loss of control, macromolecular engineering remained possible and relatively well-defined fluoropolymer-based architectures were synthesized. However, a better controlled homopolymerization of VDF was observed when Cobalt-Mediated Radical Polymerization was used.[6]

[1] Soulestin, T.; Ladmiral, V.; Domingues Dos Santos, F.; Améduri, B. (2017). Vinylidene fluoride and trifluoroethylene-containing fluorinated electroactive copolymers. How does chemistry impact properties? *Prog. Polym. Sci.*, 72, 16–60.

[2] Guerre, M.; Campagne, B.; Gimello, O.; Parra, K.; Améduri, B.; Ladmiral, V. (2015). Deeper Insight into the MADIX Polymerization of Vinylidene Fluoride. *Macromolecules*, 48 (21), 7810-7822.

[3] Bouad, V.; Guerre, M. ; Totée, C. ; Silly, G. ; Gimello, O. ; Améduri, B. ; Tahon, J-F. ; Poli, R. ; Barrau, S. ; Ladmiral, V. (2021). RAFT Polymerisation of Trifluoroethylene: The importance of understanding reverse additions. *Polym. Chem.*, 12, 2271 - 2281.

[4] Banerjee, S.; Bellan, E. V.; Gayet, F.; Debuigne, A.; Detrembleur, C.; Poli, R.; Améduri, B.; Ladmiral, V. (2017). Bis(formylphenolato)cobalt(II)-Mediated Alternating Radical Copolymerization of tert-Butyl 2-Trifluoromethylacrylate with Vinyl Acetate. *Polymers*, 9(12), 702.

[5] Guerre, M.; Rahaman, S. M. W.; Améduri, B.; Poli, R.; Ladmiral, V. (2016). Limits of Vinylidene Fluoride RAFT Polymerization. *Macromolecules,* 49 (15), 5386-5396.

[6] Banerjee, S.; Ladmiral, V.; Debuigne, A.; Detrembleur, C.; Poli, R.; Améduri, B. (2018). Organometallic Mediated Radical Polymerization of Vinylidene Fluoride. *Angew. Chem. Int. Ed.,* 57 (11), 2934-2937.