Catalyse Polymérisation Procédés et Matériaux (CP2M)

Macromolecular architectures based on polyethylene by free radical polymerization

Despite its industrial importance, ethylene remained for a very long time one of the last monomers the free radical polymerization of which could not be controlled. This would indeed allow to achieve original architectures based on polyethylene (PE) such as block copolymers exhibiting unique antagonistic, complementary or cooperative properties.

Recently, CP2M/PCM showed that controlled radical polymerization (CRP) techniques based on a reversible degenerative chain transfer were excellent tools to control the free radical polymerization of ethylene as long as the conditions were adequately chosen. We were the first to show that RAFT, a CRP technique based on the use of thiothiocarbonylated controlling agents, can successfully controlled ethylene polymerization[1] while suffering side reactions. We further showed that these side reactions could be strongly alleviated with adapted RAFT systems[2] or by using another CRP technique (TERP) based on the use of organotellerium compounds as controlling agents, works performed in collaboration with the inventor of TERP (Prof. S. Yamago, University of Kyoto, Japan) [3]. Based on these first successful investigations, we successfully performed during the last three years CRP of ethylene using iodo alkyls via a technique based on iodine transfer polymerization (ITP)[4,] and again based on reversible degenerative transfer.

These works dedicated to the controlled polymerization of ethylene, and more generally speaking this new area of research, have also considered these concepts in dispersed media.[5] They were recognized by the international scientific polymer community *via* VIP[1] or hot[5] publications in Angewandte Chemie, Journal but also by world leader researchers in the field of CRP.[6]

Strong of the understanding of these systems and their underpinning mechanisms, we now want to push forward the potential of these systems to design macromolecular architectures based on polyethylene segments. Besides, very recently, we launched a collaboration with group of Prof. Dave Haddleton (University of Warwick, UK) expert in CRP of more conventional monomers. We showed that the use of poly(methyl methacrylate) (PMMA) carrying a specific double bond on one chain end and obtained by CRP can be advantageously used as additives in the simple free radical polymerization of ethylene to produce unprecedented PMAA-*b*-PE block copolymers.[7]

The present project will thus be fully part of these different strategies and international collaborations and is thus a great opportunity for the applicant to work in a substantive research in an area largely unexplored with high applicative and bibliometric impacts.

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