From Telomerization to Controlled Radical Polymerization of Vinylidene Fluoride and Applications Therefrom

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Fluoropolymers [1] exhibit remarkable properties, which enable them to find out a wide range of High-Tech applications (cladding and cores of optical fibers, thin films for microelectronics, repellent coatings, lubricants, surfactants, fire fighting agents, membranes for fuel cells and dielectric films). Various strategies of syntheses from original telomers toward controlled fluoropolymers are depicted in this presentation.

1) First, **telomerization** [1] involves a telogen or a transfer agent (X-Y), and one or more (n) molecules of a polymerizable compound M (called taxogen or monomer), under radical polymerization conditions, leading to X-$(M)_n$-Y telomers, as follows:

$$X{-}Y + nM \xrightarrow{\text{free radicals}} X{-}(M)_n{-}Y$$

Various examples of telomerization of vinylidene fluoride, VDF ($H_2C{=}CF_2$) involving different X-Y transfer agents (hydroxylated [2], phosphonated [3], halogenated [4]) have been investigated. The kinetics of telomerization enabled us to assess the transfer constants to the telogens [1] and an increasing series regarding the efficiency of these transfer agents is supplied, correlated with the bond dissociation energy of the cleavable bond of the telogens [1]:

$CF_3CH_2OH < CH_3OH < CCl_3H < CCl_4 < (EtO)_2P(O)H < BrCF_2CFClBr < CCl_3Br < RSH < ICl$

2) The second part deals with the **applications** of these functional telomers as potential intermediates for the synthesis of well-architectured fluoropolymers including *telechelics* [1,5], *block copolymers* [1,6-9], *macromonomers* [1,10], *graft copolymers* [11]. Various examples are supplied to understand the wide potential of applications of these fluoropolymers and examples concern the use of novel oligo(VDF)-containing acrylates as *surface modifiers* [11,12], potential non-bioaccumulable surfactants,[13] or original telomers based on VDF, TFE and HFP for *hybrid fluorosilicones* [1,14].

3) Third, **Iodine transfer polymerization** (ITP [14]) and **MADIX polymerization** of vinylidene fluoride (VDF) [9,15] have been used for the controlled radical polymerization (CRP) of VDF.

Industrial applications from CRP of fluoroalkenes (e.g., surface modifiers, solvents for Lithium ion batteries, fluorosilicones, and thermoplastic elastomers) will illustrate this presentation.

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