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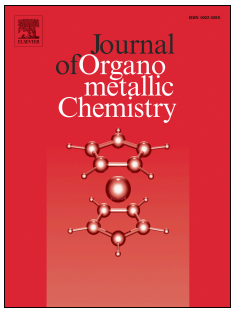

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Rinaldo Poli, S.M.Wahidur Rahaman, Vincent Ladmiral, Bruno Ameduri

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Effect of α- and β-H/F substitution on the homolytic bond strength in dormant species of controlled radical polymerization: OMRP *vs.* ITP and RAFT

Rinaldo Poli,*[a,b] S. M. Wahidur Rahaman,[a] Vincent Ladmiral, [c] Bruno Ameduri[c]

[a]*CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT, 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France CNRS. Fax: +33-561553003; Tel: +33-561333174; E-mail:rinaldo.poli@lcc-toulouse.fr.*

[b] *Institut Universitaire de France, 1, rue Descartes, 75231 Paris Cedex 05, France.*

[c] *Ingénierie et Architectures Macromoléculaires, Institut Charles Gerhardt, UMR 5253 CNRS, UM, ENSCM, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France*

Abstract

The X-C bond dissociation energies (BDEs) for five series of X-$CH_{2-n}F_nCH_{3-m}F_m$ molecules (n = 0, 1, 2; m = 0, 1, 2, 3) with X = H, I, SC(S)OEt, $Co(acac)_2$ or $Mn(CO)_5$ were calculated using a DFT approach, yielding results in good agreement with the few experimentally determined values (X = H and I). Calculations were also carried out on the simpler $(CO)_5Mn$-CF_nH_{3-n} molecules (n = 0, 1, 2, 3), for which experimental data are available. The BDE trends as n and m vary are different for different X groups: BDE increases as n increases (particularly from 0 to 1) for X = H, I and SC(S)OEt, but decreases (particularly from 1 to 2) for X = $Co(acac)_2$ and $Mn(CO)_5$. The effective charge analysis suggests that the effect of the bond polarity on the ionic component of the bond energy is a major contriution to these trends. These results rationalize the limited control, for the polymerization of vinylidene fluoride (VDF), by the iodine transfer polymerization (ITP) and reversible addition-fragmentation chain-transfer (RAFT) polymerization approaches. They also predict a better controlled process for this monomer by organometallic mediated radical polymerization (OMRP), mediated by $Co(acac)_2$. They also allow predictions for the performance of the same processes for other fluorinated monomers. The results for X = $Mn(CO)_5$ suggest that the $(CO)_5Mn$-$CH_{2-n}F_nCH_{3-m}F_m$ molecules cannot be thermally activated at significant rates. Therefore, they either do not form or are photochemically reactivated during the $Mn_2(CO)_{10}$-assisted ITP polymerization of VDF.

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