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Grafting from Fluoropolymers Using ATRP: What is Missing?

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Dedicated to Professor Rinaldo Poli on the occasion of his 65th birthday

ATRP

Dehydrofluorination

Fluoropolymers

Grafting-from

strategy

PVDF

Grafting-from ATRP protocols using fluoropolymers as substrates are very often used. Actual positive proof that ATRP is the mechanism at work in the grafting or that grafting occurred at all is very scarce. This perspective article gives an overview of the most relevant examples of such protocols as well as possible other mechanisms of grafting.

Grafting polymers from fluoropolymer backbones is very advantageous to modify the properties of these often non-functional materials. It is particularly useful in the field of ultrafiltration membranes to tune the hydrophilicity of PVDF membranes and to add other properties such as antifouling for example. One of the main techniques used to effect such grafting is ATRP. A large number of papers are published every year on this topic. However, careful examination of this body of work reveals that the evidence provided to support the covalent bonding of polymer chains on the fluoropolymers are often limited and rather unconvincing. This is of course due to the difficult detection of the rare connecting covalent bonds. Nevertheless, this detection problem is not the only issue. Grafting from fluoropolymers using ATRP relies on the homolytic cleavage of C-C-F bond, notorious for their high stability and BDE. Moreover, fluoropolymers based on VDF are prone to dehydrofluorination by reaction with bases and nucleophiles, which leads to the formation of unsaturations within the polymer backbone. This reaction is often completely ignored even though ATRP ligands can trigger this elimination. These two very often overlooked reactivity

features seriously question the use of ATRP as an efficient grafting technique for fluoropolymers.

Atom Transfer Radical Polymerization (ATRP) is a very powerful and versatile Reversible Deactivation Radical Polymerization (RDRP) technique. Careful choice of the metal (Cu, Ru, Fe, Mo, Os...), ligand and technique variant (ICAR, SARA-ATRP, AGET, ARGET, e-ATRP...) allow the control of a very large range of vinyl monomers under a wide range of polymerization conditions (bulk, solution, dispersed media, protic solvents...).^[1,2] ATRP got a long way since its beginnings in the mid-1990s with the initial Ruthenium/triphenylphosphine^[3] and Copper/2,2'-bipyridine^[4] catalytic systems used to demonstrate the controlled radical polymerization of methyl methacrylate. The following decades saw an explosion of the research dedicated to RDRP in general and ATRP in particular with considerable efforts devoted to the expansions of the range of monomers that could be polymerized, the range of polymer architectures that could be synthesized, the range of solvents, metals or polymerization processes that could be used, the decrease of the amount of catalyst needed, the search for more active catalysts, the elimination of side reactions, and in general the better understanding of the ATRP mechanism.^[5,6] While Professor Rinaldo Poli made remarkable contributions to Organometallic-Mediated Radical Polymerization (OMRP),^[7,8] his research also had significant impact on ATRP. From a mechanistic point of view, R. Poli's work shed some light on the complex interplay at work between ATRP, OMRP (both Reversible Termination and Degenerative Transfer variants) and Chain Transfer-Catalyzed Radical Polymerization (CTCRP)^[9,10,11] as well as on the side reactions such as catalytic radical termination that do occur during ATRP.^[12,13] He also participated to important breakthrough on the Copper-catalyzed ATRP such as the discovery of the most active copper ATRP catalyst based on tris[(4-dimethylaminiopyridyl)methyl]amine (TPMANMe₂) as ligand.^[14] In addition to his work on Copper catalysts, he also largely contributed to examine other metals for ATRP such as Osmium,^[15] Molybdenum^[16] or Iron.^[17,18] If ATRP is now amenable to a very large range of monomers, it so far failed to polymerize fluorinated olefins (i.e. monomers bearing fluorine atoms or trifluoromethyl

groups on the vinyl carbons). Indeed, these monomers have, so far, only been polymerized using degenerative transfer radical polymerization techniques such as Iodine Transfer Polymerization (ITP)^[19] or Reversible Addition-Fragmentation chain Transfer (RAFT)^[20] although R Poli led the first forays in the OMRP of vinylidene fluoride (VDF).^[21,22] VDF (1,1-difluoroethene), the most emblematic and likely among the easiest fluoromonomers to polymerize, features a peculiar and not well understood reactivity. For example, its polymerization is not initiated with usual azo initiator, but instead requires the use of peroxide or peroxodicarbonates (i.e. initiator leading to oxygen-centered radicals). The reason why ATRP does not operate with VDF is not completely understood either, but a few studies have provided some insights.^[23] Initiation and activation are problematic. Indeed, perfluoroalkyl bromides have been shown to be about 100 times less reactive than brominated esters typically used in ATRP.^[24] Likewise DFT calculations placed the ATRP equilibrium constant for the homolytic bond cleavage of $\text{CH}_3\text{CF}_2\text{-X}$ ($\text{X}=\text{C}=\text{Cl}, \text{Br}$) at least 7 orders of magnitude lower than that of methyl 2-halopropionate.^[25] In addition, VDF is prone to reverse additions which under RDRP conditions invariably produce two different dormant species possessing very different reactivities towards reactivation which leads to gradual loss of control of the polymerization.^[26] This phenomenon was largely documented over the last 5 years in articles reporting the results of the work undertaken in collaboration with R. Poli on the RAFT polymerization of fluoroolefins,^[27,28,29] and the synthesis of PVDF-containing block copolymers.^[30]

PVDF and copolymers of VDF are very interesting materials which have found numerous applications. They are, for example, very important materials for ultrafiltration membranes owing to their high chemical resistance and mechanical properties allowing relatively easy clean-up procedures and low energy consumption.^[31] These fluoropolymers are also endowed with high electroactive properties^[32] such as ferroelectricity, pyroelectricity and piezoelectricity, which make them very good candidates for emerging applications in the fields of haptics and printed electronics.^[33] Advanced synthetic techniques permitting a better control of the topology, and functionalization of these VDF-containing polymers could open

new opportunities to better performing applications. UF membranes featuring a higher density of pores of uniform size, and/or possessing available functional groups would undoubtedly be very advantageous in terms of energy consumption and permeance, or selectivity.^[34] Similarly, well defined PVDF-based block copolymers (and other architectures) could bring about new possibilities in the field of electroactive polymers and composites.^[35] So far ITP,^[26] RAFT^[20] and to a lesser extent Cobalt-Mediated Radical Polymerization (CMRP)^[21,22] have been mainly used to successfully prepare functional or well-defined PVDF-based architectures. CMRP in particular was demonstrated to largely mitigate or even overcome completely the issue caused by the existence of two different PVDF dormant species due to reverse addition.^[21] ATRP is however often reported as an efficient technique to prepare graft copolymers from fluoropolymers. A large number of papers indeed report the surface modification of fluoropolymer (mainly for membrane filtration application) via ATRP.^[36] The vast majority of these papers focus on the properties of the resulting surfaces and materials. Only a few articles address the actual ATRP process supposedly occurring on fluoropolymers. The feasibility of ATRP from fluoropolymers is however not obvious and has rarely been fully and convincingly investigated. The present perspective article will first give a brief overview of the most representative articles that report the use of ATRP to graft polymer chains from fluoropolymers and will then underlines the important reactivity notions that should be taken into account when attempting ATRP from fluoropolymers.

ATRP using PVDF Homopolymers

The earliest report on the use of ATRP with PVDF was published by Shi et al. in 1999 and concerns the synthesis of PVDF-containing block copolymers. They first prepared a bromine terminated PVDF by radical telomerization, using di-*tert*-butylperoxide as initiator, and 1,2-dibromotetrafluoroethane as telogen. This PVDF telechelic initiator was then used as a macro-initiator to polymerize styrene (S) under ATRP regime using CuBr/bpy at 110°C. The analysis of the resulting PS-*b*-PVDF-*b*-PS triblock copolymer by NMR and SEC confirmed the controlled character of the polymerization (controlled molar mass and low

dispersity).^[37] In a similar manner, Laruelle and co-workers produced a CCl_3 -functionalized PVDF via radical telomerization of VDF with chloroform. This PVDF macro-initiator was used to polymerize styrene sulfonate in the presence of CuCl and PMDETA. The PVDF macro-initiator showed a high blocking efficiency as the GPC traces did not show any trace of remaining homo PVDF chains.^[38] Paeng and co-workers, prepared di- and triblock copolymers from monofunctional and difunctional PVDF, synthesized via iodine transfer polymerization (ITP). Methyl methacrylate (MMA) was polymerized at 90°C in the presence of mono or di- iodinated PVDF macro-initiators and CuCl/bpy catalyst. These ATRP protocols based on the initiations from $\text{CF}_2\text{-I}$ and $\text{CH}_2\text{-I}$ groups led to PVDF/PMMA diblock and triblock copolymers. However, the initiating efficiency was poor, and the block copolymers showed high dispersity.^[39]

The very first example of a graft copolymer prepared from PVDF was reported by Boutevin et al. in 2006.^[40] Polystyrene was grafted from a PVDF macroinitiator bearing brominated side groups synthesized by radical copolymerization of VDF and 8-bromo-1H,1H,2H-perfluorooct-1-ene (BDFO). This fluorinated macroinitiator along with CuBr/HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine) catalyst was used to polymerize styrene via a grafting-from approach. The linear dependence of the evolution of the molar masses vs styrene conversion, combined with the decrease of the dispersity indicated a controlled behavior for the grafting-from ATRP polymerization. Nandi et al. also reported a grafting-from strategy for the polymerization of a range of monomers from PVDF via the combination of atom transfer radical coupling (ATRC) and atom transfer radical polymerization (ATRP).^[41,42,43] In this approach, 4-hydroxy TEMPO moieties were anchored onto the PVDF chains by substitution of fluorine atom on the PVDF chains by ATRC using CuCl/DMDP (dimethyl-2,2'-dipyridyl) catalyst at 90°C . The pendant hydroxyl groups present at the tethered TEMPO moieties were then reacted either with 2-bromoisobutyryl bromide, 2-bromopropionyl bromide or 2-chloropropionyl chloride to produce various macro-initiators. Relatively high grafting densities and molar masses were achieved for methacrylates (MMA, DMAEMA, tBMA and MeO_2MA), acrylates (nBA and tBA) and

acrylamides (DMA) polymerized using CuCl/4,4-dimethyl-2,2'-dipyridyl (DMDP), CuBr/DMDP, and CuCl/Me₆TREN respectively. The authors claimed that the ATRC occurred preferentially on the fluorine atoms of the minority CF₂-CF₂ motifs of PVDF caused by head-to-head addition. In addition to the strategy consisting in installing initiating moieties on a PVDF backbone, direct ATRP from PVDF relying on the homolytic cleavage of C<C->F bonds for initiation has been reported. In 2002, Mayes reported the first example of such C<C->F initiated ATRP from PVDF.^[44] In this study, PVDF-*g*-POEM (POEM=poly(oxyethylene methacrylate) and PVDF-*g*-PtBMA were prepared using CuCl/DMDP in NMP at 90°C. The graft copolymers were characterized using ¹H NMR and SEC. The authors claimed successful grafting by the fact that SEC chromatograms of the grafted polymers before and after prolonged extraction with a good solvent for POEM were identical. Other examples of this direct ATRP from PVDF strategy (i.e. relying on initiation via C<C->F bond homolytic cleavage) report the grafting of PDMAEMA,^[45] PGMA,^[46] PnBMA^[47] and P(tBAEMA-*co*-OEGMA)^[48] chains from PVDF using CuCl/DMDP in NMP at 90°C. Noticing that PVDF offers different types of initiating sites with different reactivity, namely the head-to-head (HH, produced by reverse addition leading to CF₂CF₂ motifs) and head-to-tail (HT, resulting from regular additions and generating CF₂-CH₂ motifs) sequences, Nandi and coworkers^[45] claimed that the HH sites (representing about 4.33 mol.% of the total number of additions) are better initiating sites than the HT motifs. They justified their claims by monitoring the decrease of the proportion of H<C->H ¹⁹F NMR signals compared to that of HT resonances. AGET-ATRP has also been used on PVDF using the C<C->F bonds as initiating sites. Iron-mediated AGET-ATRP was performed with methyl methacrylate (MMA) and poly (ethylene glycol) methyl ether methacrylate (PEGMA) as the monomers, FeCl₃ as the catalyst, triphenylphosphine (PPh₃) as the ligand, and ascorbic acid as the reducing agent in the presence of limited amounts of air. The resulting graft copolymers (PVDF-*g*-PMMA and PVDF-*g*-PPEGMA) were only characterized using ¹H NMR, FTIR and X-ray photoelectron spectroscopy, providing little evidence that the grafting actually took place from the C<C->F sites on the PVDF backbone.^[49] PVDF-*g*-PPEGMA prepared via

photoredox mediated ATRP using Ir(ppy)₃ as catalyst and blue LEDs was also reported by Huang et al.,^[50] although proof of grafting were rather weak (¹H NMR only).

ATRP from Fluorocopolymers

The grafting of polymer chain from VDF-containing copolymers using C<C>F bonds as the initiating sites were also reported.

P(VDF-*co*-HFP)

The grafting from poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-*co*-HFP)) copolymer was reported in a couple of publications. Poly(ethylene glycol) methyl ether methacrylate (PEGMA) was allegedly grafted from P(VDF-*co*-HFP)) copolymer via ATRP in DMF at 120^oC using CuBr/ HMTETA as the catalyst.^[51] Little evidence of grafting were provided and the density of grafting was very low. Butyl acrylamide was also allegedly grafted from P(VDF-*co*-HFP) chain using ATRP at room temperature.^[52] Very little experimental details were given and proof of grafting were not provided. However, this paper describes the formation of double bond within the fluoropolymer backbone by dehydrofluorination upon reaction with a strong base.

P(VDF-*co*-TrFE)

Takahara et al. reported the grafting of poly(vinylidene fluoride-*co*-trifluoroethylene) (P(VDF-*co*-TrFE) copolymers with PtBA chains using ATRP.^[53] The experiments were carried out in DMF at 85^oC using CuCl/PMDETA as catalyst. Remarkably this article is one of the very few to present and exploit ¹⁹F NMR spectroscopy to attempt to prove grafting. According to the authors grafting only occurred on the CF₂ units of TrFE. However, given the very small quantity of grafting and fairly subtle and difficult to interpret changes in the ¹⁹F NMR spectra of the copolymers, these results would need to be confirmed.

NAFION

A few articles report the use of ATRP to graft polymers from NAFION (a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxo-4-methyl-7-octene-sulfonic acid). The authors claim to effect the grafting of PNIPAM (CuCl/Me₆TREN, room temperature), PS (CuBr/bpy, 80[°]C), poly(1-vinylimidazole) (CuBr/bpy, 80[°]C), PSS (CuBr/bpy, 80[°]C) and poly(2-trimethylammonium chloride ethyl methacrylate) (PMETAC, CuBr/bpy, 80[°]C) from the C<C>F bonds of Nafion.^[54,55,56] However, the authors provided very little evidence of grafting.

P(VDF-*co*-CTFE)

Copolymers of VDF and chlorotrifluoroethylene (CTFE) were also used as substrate for ATRP. In this case the C<C>Cl bonds of CTFE were used as the initiating sites.

Russell and co-workers, grafted polystyrene (PS) and poly(tert-butyl acrylate) (PtBA) from poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (P(VDF-*co*-CTFE)) via ATRP using CuCl/Bpy at 120[°]C or CuCl/PMDETA at 90[°]C in NMP.^[57] The authors provided limited spectroscopic evidence of grafting. A similar approach was used to synthesize amphiphilic PVDF-*g*-PEGMA or PVDF-*g*-PSS (via sulfonation of the polystyrene moieties^[58,59] using CuCl/bpy in NMP at 110[°]C.^[60] Photo-mediated metal-free ATRP using 10-Methylphenothiazine was also employed to polymerize MMA from P(VDF-*co*-CTFE) using the CTFE C<C>Cl bond as the grafting site.^[61] However, the evidence of grafting were quite thin. Photo-induced p-anisaldehyde-catalyzed ATRP was used to graft poly(methyl methacrylate) (PMMA) and poly(glycidyl methacrylate) (PGMA) from P(VDF-*co*-CTFE) under UV irradiation using low catalyst concentration. Chain extension was performed to confirm the availability of the chlorine atom on the grafted polymer chain end. Metal-free P(VDF-*co*-CTFE)-*g*-PMMA and P(VDF-*co*-CTFE)-*g*-PGMA with varied graft contents were reported.^[62] However, once again unambiguous spectroscopic proof of the grafting were not provided although ¹⁹F NMR spectroscopy was used.

P(VDF-*ter*-TrFE-*ter*-CTFE)

Harnessing the potential homolytic cleavage of the C<C->Cl bond of CTFE units, PMMA or PEMA were grafted from P(VDF-*ter*-TrFE-*ter*-CTFE) terpolymer via ARGET-ATRP using CuCl/ Cu/ Bpy catalytic system and NMP as solvent.^[63,64] A very similar procedure was used to polymerise methyl methacrylate and styrene in a two-step process from the CTFE units of the fluoroterpolymer.^[65] Evidence of grafting were mainly derived from ¹H NMR spectra.

The issues of ATRP from fluoropolymers

The above-mentioned articles report the grafting of polymer chains on fluoropolymers using ATRP and are representative of the state of the art in this subfield. Many more articles rely on this technique to produce grafted fluoropolymers mainly for films and membrane application, but these articles give very few details or evidence on the grafting at the molecular scale.

Activation of C<C->F and C<C->Cl linkages in PVDF- and PCTFE-based copolymers is the most widely used technique to graft polymer chains onto fluoropolymers. If the C<C->Cl bonds of CTFE is probably activatable using ATRP catalysts, the activation of C<C->F bonds is more problematic.

Confronted to the uncertainties regarding the possibility of using the C<C->F bond as initiation site for ATRP,^[66] Scialdone carried out an electroanalytical investigation of the ATRP from PVDF and PVC.^[67] Grafting-from experiments were performed in NMP at temperature ranging from 45 to 90°C, using hydroxyethyl methacrylate (HEMA) as monomer, CuCl or CuBr as the metal salt and TPMA or Me₆TREN as ligand, and were further supported by cyclic voltammetry measurements of the redox potentials of the catalysts used. These experiments showed that while PVC could be activated at moderate temperature by the two catalysts, activation of the C<C->F bond of PVDF could only be achieved using Cu/Me₆TREN at high temperature (90°C), and only afforded low degree of grafting (<5%).

Indeed, fluorine is the most electronegative element and when it is bounded to a carbon atom results into the strongest bonds found in organic chemistry^[68] with a bond

dissociation energy of $105.4 \text{ kcal mol}^{-1}$ (in comparison $\text{BDE}_{\text{C-H}} = 98.8 \text{ kcal mol}^{-1}$ and $\text{BDE}_{\text{C-Cl}} = 78.5 \text{ kcal mol}^{-1}$). Based solely on these BDE values, and, considering the much higher stability of C-C-F bonds in comparison to C-C-H bonds, it may be possible that the grafting reportedly due to C-C-F activation proceeds instead via C-C-H activation.^[69] To the best of our knowledge, only one article examined the activation of C-C-F bond by ATRP catalysts. Matyjaszewski and co-workers evaluated the possibility to initiate an ATRP from a C-C-F bond.^[70] The thermodynamics and kinetics of C-C-F bond activation by ATRP were carefully investigated using different initiators, catalysts and compared to other C-halogen bonds. It was shown that the bond dissociation energy (BDE) of several benzyl halides (X=F, Cl, Br, I) representing the strength of the C-C-X bond and the relative affinities of Cu^{II} and Cu^{I} increased in the order $\text{I} < \text{Br} < \text{Cl} < \text{F}$. (Figure¹.) The high bond dissociation energy of benzyl fluoride ATRP initiator induces considerably low $K_{\text{ATRP,F}}$ meaning that the C-C-F activation is expected to be rather slow with low radical concentration generated. Therefore, the activation and deactivation processes might be possible, although unfavored, with some chain grafting but the control of the polymerization should be really poor. The slow activation and deactivation processes would indeed generate ill-defined structures. The authors also showed that C-C-F activation was possible with more activated structures such as diethyl fluoromalonate with good efficiency (Styrene, 95%). However, M_n did not increase with conversion, suggesting slow deactivation/reactivation of radicals and limited control. In conclusion, F-bearing initiators might be activated by ATRP, but would require very active ATRP catalysts. Direct activation from PVDF or other F-bearing polymer backbones is thus not only difficult (i.e. leading to low degree of grafting), but would also not proceed with good control under ATRP conditions.

The same authors also suggested that C-C-H activation is not possible since $\text{Cu} < \text{C} > \text{H}$ interaction is much weaker than $\text{Cu} < \text{C} > \text{X}$ affinity and would result in $\text{Cu}^{\text{II}} < \text{C} > \text{hydride}$ complex with thermodynamically unfavorable step.

In addition to the difficult activation of C-C-F bonds, fluoropolymers such as PVDF-based copolymers are prone to dehydrofluorination in the presence of bases or nucleophiles (Figure 2).^[71] PVDF solutions readily turn red then black as a result of dehydrofluorination reactions generating conjugated C=C bonds within the PVDF backbone.^[72] Only 0.1% of dehydrofluorination is sufficient to macroscopically observe full coloration of the polymer.^[73] This side reaction was observed many times in the presence of bases such as amines^[74,75] or K₂CO₃.^[76] The poor stability of PVDF-based copolymers in the presence of bases considerably restrain post-functionalization possibilities. This side reaction was even observed in the presence of phenoxide, especially used to prevent dehydrofluorination reactions, with percentage of double bonds up to 14%.^[77] Nonetheless, dehydrofluorination reactions were purposely used for the crosslinking of PVDF-based fluoroelastomers.^[74] Various procedures were reported either using diamine following a two-step procedure (dehydrofluorination+Michael Addition) or via the use of bisphenol. Wu and co-workers for example exploited this dehydrofluorination reaction assisted with ammonia to prepare PVDF and Nafion crosslinked composites for proton exchange membranes.^[78] This strategy was also used for the preparation of PVDF electrospun fibers improving processability (lower viscosity) as well as improved piezoelectric properties. This reaction is almost always completely neglected in the papers dealing with the grafting of fluoropolymers via ATRP although this side reaction is expected to occur in the presence of ATRP ligands since they are organic bases. The formation of unsaturations on the fluoropolymer backbone upon action of the ATRP ligands (often used in slight excess) could also explain the observed grafting. Indeed, these double bonds can react in the presence of radicals leading to the desired grafting. The grafting would thus proceed via grafting-through rather than grafting-from. This pathway proceeding via the reaction of in-situ formed double bonds in the fluoropolymer backbone could also explain the formation of gels that is often observed during the ATRP grafting-from of fluoropolymers. Since ligands are usually used in low quantity, the formation of C=C double bonds in combination with the little activation of C-C-F bonds might be enough to generate the grafting reported in the papers. However, the grafting

efficiency as well as degree of grafting are low and difficult to control. Therefore, this strategy produces ill-defined macromolecular architectures with very low control of grafting density and polymer definition.

Conclusions

The vast majority of the papers dealing with the grafting of polymer chains on fluoropolymers using ATRP are rather unconvincing. They, for the most part, completely ignore important chemical reactions at the heart of the system they use: First the very difficult activation of C<C->F bonds which is the most robust bond in organic chemistry, and which can, as such only be activated using very efficient ATRP catalysts; second, the slow deactivation of the radicals by F-bearing ATRP catalysts (although this phenomenon is however often likely mitigated by the use of CuCl or CuBr as metal source which should favor halogen exchange, and lead to Cl- or Br- terminated dormant chain easier to activate and deactivate.); and third, the high propensity of fluoropolymers based on VDF to undergo dehydrohalogenation (mainly dehydrofluorination) leading to carbon-carbon double bonds within the fluoropolymer backbone, which can effect the desired grafting via a grafting-through mechanism. In addition, most reports so far, provide very little convincing evidence of the actual grafting. Most papers rely on ^1H NMR rather than ^{19}F NMR which is rather surprising since the topic of the papers are fluoropolymers. Even more surprising, ^{13}C NMR is never used although the C<C->F activation would likely be more easily detected using ^{13}C NMR signals than any other nucleus. In conclusions, although the grafting of polymer chains from fluoropolymers has been reported in numerous articles, the exact chemistry at work in these papers and the identification of the chemical bonds involved in the grafting in the different systems reported are not clear.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

<lit1><jnl>X. Pan, M. Fantin, F. Yuan, K. Matyjaszewski, *Chem. Soc. Rev.* **2018**, *47*, 5457--5490</jnl>.

<lit2><jnl>K. Matyjaszewski, *Macromolecules* **2012**, *45*, 4015--4039</jnl>.

<lit3><jnl>M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721--1723</jnl>.

<lit4><jnl>J<C->S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614--5615</jnl>.

<lit5><jnl>D. Konkolewicz, P. Krys, K. Matyjaszewski, *Acc. Chem. Res.* **2014**, *47*, 3028--3036</jnl>.

<lit6><jnl>D. Konkolewicz, Y. Wang, P. Krys, M. Zhong, A.^{^^}A. Isse, A. Gennaro, K. Matyjaszewski, *Polym. Chem.* **2014**, *5*, 4396--4417</jnl>.

<lit7><jnl>R.Poli, *Chem. Eur. J.* **2015**, *21*, 6988--7001</jnl>.

<lit8><jnl>R. Poli, S.^{^^}M.^{^^}W. Rahaman, V. Ladmiral, B. Ameduri, *J. Organomet. Chem.* **2018**, *864*, 12--18</jnl>.

<lit9><jnl>R. Poli, *Eur. J. Inorg. Chem.* **2011**, *10*, 1513--1530</jnl>.

<lit10><jnl>Y. Champouret, K.^{^^}Cory Macleod, K. Smith, B. Patrick, R. Poli, *Organometallics* **2010**, *29*, 3125--3132</jnl>.

<lit11><jnl>R. Poli, M. Shaver, *Chem. Eur. J.* **2014**, *20*, 17530--17540</jnl>.

<lit12><jnl>T.^{^^}G. Ribelli, K.^{^^}F. Augustine, M. Fantin, P. Krys, R. Poli, K. Matyjaszewski, *Macromolecules* **2017**, *50*, 7920--7929</jnl>.

<lit13><jnl>M. Fantin, F. Lorandi, T. Ribelli, G. Szczepaniak, A. Enciso, C. Fliedel, L. Thevenin, A.^{^^}A. Isse, R. Poli, K. Matyjaszewski, *Macromolecules* **2019**, *52*, 4079--4090</jnl>.

- <lit14><jnl>T.[^]G. Ribelli, M. Fantin, J<C->C. Daran, K.[^]F. Augustine, R. Poli, K. Matyjaszewski *J. Am. Chem. Soc.* **2018**, *140*, 1525--1534</jnl>.
- <lit15><jnl>W. Braunecker, W. Brown, B. Morelli, W. Tang, R. Poli, K. Matyjaszewski, *Macromolecules* **2007**, *40*, 8576--8585</jnl>.
- <lit16><jnl>S. Maria, F. Stoffelbach, J. Mata, J<C->C. Daran, P. Richard, R. Poli, *J. Am. Chem. Soc.* **2005**, *127*, 5946--5956</jnl>.
- <lit17><jnl>J. Wang, J. Han, X. Xie, Z. Xue, C. Fliedel, R. Poli, *Macromolecules* **2019**, *52*, 5366--5376</jnl>.
- <lit18><jnl>R. Poli, L.[^]E.[^]N. Allan, M.[^]P. Shaver, *Prog. Polym. Sci.* **2014**, *39*, 1827--1845</jnl>.
- <lit19><jnl>G. David, C. Boyer, J. Tonnar, B. Ameduri, P. Lacroix-Desmazes, B. Boutevin, *Chem. Rev.* **2006**, *106*, 3936--3962</jnl>.
- <lit20><jnl>M. Guerre, B. Campagne, O. Gimello, K. Parra, B. Améduri, V. Ladmiral, *Macromolecules* **2015**, *48*, 7810--7822</jnl>.
- <lit21><jnl>S. Banerjee, V. Ladmiral, A. Debuigne, C. Detrembleur, R. Poli, B. Améduri, *Angew. Chem. Int. Ed.* **2018**, *57*, 2934--2937; *Angew. Chem.* **2018**, *130*, 2984--2987</jnl>.
- <lit22><jnl>P.[^]G. Falireas, V. Ladmiral, A. Debuigne, C. Detrembleur, R. Poli, B. Ameduri, *Macromolecules* **2019**, *52*, 1266--1276</jnl>.
- <lit23><jnl>A.[^]D. Asandei, *Chem. Rev.* **2016**, *116*, 2244--2274</jnl>.
- <lit24><jnl>L. Sauguet, C. Boyer, B. Ameduri, B. Boutevin, *Macromolecules* **2006**, *39*, 9087--9101</jnl>.
- <lit25><jnl>M.[^]B. Gillies, K. Matyjaszewski, P.[^]O. Norrby, T. Pintauer, R. Poli, P. Richard, *Macromolecules* **2003**, *36*, 8551--8559</jnl>.
- <lit26><jnl>A.[^]D. Asandei, O.[^]I. Adebolu, C.[^]P. Simpson, *J. Am. Chem. Soc.* **2012**, *134*, 6080--6083</jnl>.

- <lit27><jnl>M. Guerre, S.^M.^W. Rahaman, B. Améduri, R. Poli, V. Ladmiral, *Macromolecules* **2016**, *49*, 5386--5396</jnl>.
- <lit28><jnl>V. Bouad, M. Guerre, C. Totée, G. Silly, O. Gimello, B. Améduri, J<C->F. Tahon, R. Poli, S. Barrau, V. Ladmiral, *Polym. Chem.* **2021**, *12*, 2271--2281</jnl>.
- <lit29><jnl>V. Bouad, M. Guerre, S. Zeliouche, B. Améduri, C. Totée, G. Silly, R. Poli, V. Ladmiral, *Polym. Chem.* **2021**, *12*, 2293--2304</jnl>.
- <lit30><jnl>M. Guerre, S.^M.^W. Rahaman, B. Améduri, R. Poli, V. Ladmiral, *Polym. Chem.* **2016**, *7*, 6918--6933</jnl>.
- <lit31><jnl>P. Saxena, P. Shukla, *Adv. Compos. Hybrid Mater.* **2021**, *4*, 8--26</jnl>.
- <lit32><jnl>T. Soulestin, V. Ladmiral, F. Domingues^{Dos}^{Santos}, B. Améduri, *Prog. Polym. Sci.* **2017**, *72*, 16--60</jnl>.
- <lit33><jnl>Y. Wu, Y. Ma, H. Zheng, S. Ramakrishna, *Mater. Des.* **2021**, *211*, 110164</jnl>.
- <lit34><jnl>V. Abetz, *Macromol. Rapid Commun.* **2015**, *36*, 10--22</jnl>.
- <lit35><jnl>I. Terzic, N.^L. Meereboer, M. Acuaatla, G. Portale, K. Loos, *Nat. Commun.* **2019**, *10*, 601</jnl>.
- <lit36><jnl>A. Kuila, D.^P. Chatterjee, N. Maity, A.^K. Nandi, *J. Polym. Sci. Part A* **2017**, *55*, 2569--2584</jnl>.
- <lit37><jnl>Z. Zhang, S. Ying, Z. Shi, *Polymer* **1999**, *40*, 1341--1345</jnl>.
- <lit38><jnl>G. Laruelle, E. Nicol, B. Ameduri, J<C->F. Tassin, N. Ajellal, *J. Polym. Sci. Part A* **2011**, *49*, 3960--3969</jnl>.
- <lit39><jnl>S.-M. Jo, W.-S. Lee, B.-S. Ahn, K.-Y. Park, K.-A. Kim, I.-S. Rhee^{Paeng}, *Polym. Bull.* **2000**, *44*, 1--8</jnl>.
- <lit40><jnl>L. Sauguet, C. Boyer, B. Ameduri, B. Boutevin, *Macromolecules* **2006**, *39*, 9087--9101</jnl>.

- <lit41><jnl>A. Kuila, D.[^]P. Chatterjee, R.[^]K. Layek, A.[^]K. Nandi *J. Polym. Sci. Part A* **2014**, 52, 995--1008</jnl>.
- <lit42><jnl>A. Kuila, N. Maity, D.[^]P. Chatterjee, A.[^]K. Nandi, *J. Phys. Chem. B* **2016**, 120, 2557-2568</jnl>.
- <lit43><jnl>A. Kuila, N. Maity, D.[^]P. Chatterjee, A.[^]K. Nandi, *J. Mater. Chem. A* **2015**, 3,13546</jnl>.
- <lit44><jnl>J.[^]F. Hester, P. Banerjee, Y.-Y. Won, A. Akthakul, M.[^]H. Acar, A.[^]M. Mayes, *Macromolecules* **2002**, 35, 7652--7661</jnl>.
- <lit45><jnl>S. Samanta, D.[^]P. Chatterjee, S. Manna, A. Mandal, A. Garai, A.[^]K. Nandi, *Macromolecules* **2009**, 42, 3112--3120</jnl>.
- <lit46><jnl>S. Samanta, D.[^]P. Chatterjee, R.[^]K. Layek, A.[^]K. Nandi, *J. Mater. Chem.* **2012**, 22, 10542</jnl>.
- <lit47><jnl>S. Samanta, D.[^]P. Chatterjee, R.[^]K. Layek, A.[^]K. Nandi, *Macromol. Chem. Phys.* **2011**, 212, 134--149</jnl>.
- <lit48><jnl>M. Pakhira, D.[^]P. Chatterjee, D. Mallick, R. Ghosh, A.[^]K. Nandi, *Langmuir* **2021**, 37, 4953--4963</jnl>.
- <lit49><jnl>T. Zhao, L. Zhang, Z. Zhang, N. Zhou, Z. Cheng, X. Zhu, *J. Polym. Sci. Part A* **2011**, 49, 2315--2324</jnl>.
- <lit50><jnl>Y. Que, Z. Huang, C. Feng, Y. Yang, X. Huang, *ACS Macro Lett.* **2016**, 5, 1339--1343</jnl>.
- <lit51><jnl>S. Yu, L. Chen, Y. Chen, Y. Tong, *Appl. Surf. Sci.* **2012**, 258, 4983--4989</jnl>.
- <lit52><jnl>S.[^]P. Jakriya, A.[^]M. Syed, S.[^]K. Pillai, D.[^]B. Rahim, *Mater. Express* **2018**, 8, 77--84</jnl>.
- <lit53><jnl>M. Kobayashi, Y. Higaki, T. Kimura, F. Boschet, A. Takahara, B. Améduri, *RSC Adv.* **2016**, 6, 86373</jnl>.

- <lit54><jnl>K.-J. Peng, K.-H. Wang, K.-Y. Hsu, Y.-L. Liu, *ACS Macro Lett.* **2015**, *4*, 197--201</jnl>.
- <lit55><jnl>K. Feng, L. Liu, B. Tang, N. Li, P. Wu, *ACS Appl. Mater. Interfaces* **2016**, *8*, 11516--11525</jnl>.
- <lit56><jnl>J. Dai, T. Ding, Y. Dong, X. Teng, *Ionics* **2021**, *27*, 2127--2138</jnl>.
- <lit57><jnl>M. Zhang, T.[^]P. Russell, *Macromolecules* **2006**, *39*, 3531--3539</jnl>.
- <lit58><jnl>Z. Zhang, E. Chalkova, M. Fedkin, C. Wang, S.[^]N. Lvov, S. Komarneni, T.[^]C.[^]M. Chung, *Macromolecules* **2008**, *41*, 9130--9139</jnl>.
- <lit59><jnl>A.[^]C.[^]C. Yang, R. Narimani, Z. Zhang, B.[^]J. Frisken, S. Holdcroft, *Chem. Mater.* **2013**, *25*, 1935--1946</jnl>.
- <lit60><jnl>G.[^]A. Eken, M.[^]H. Acar, *Eur. Polym. J.* **2019**, *114*, 249--254</jnl>.
- <lit61><jnl>S. Tan, J. Xiong, Y. Zhao, J. Liu, Z. Zhang, *J. Mater. Chem. C* **2018**, *6*, 4131—4139</jnl>.
- <lit62><jnl>X. Hu, N. Li, T.Heng, L. Fang, C. Lu, *React. Funct. Polym.* **2020**, *150*, 104541</jnl>.
- <lit63><jnl>J. Wang, Y. Xie, J. Liu, Z. Zhang, Y. Zhang, *Appl. Surf. Sci.* **2019**, *469*, 437--445</jnl>.
- <lit64><jnl>J. Li, S. Tan, S. Ding, H. Li, L. Yang, Z. Zhang, *J. Mater. Chem.* **2012**, *22*, 23468</jnl>.
- <lit65><jnl>J. Liu, J. Liao, Y. Liao, Z. Zhang, *Polym. Chem.* **2019**, *10*, 3547--3555</jnl>.
- <lit66><jnl>B. Améduri, *Macromolecules* **2010**, *43*, 10163--10184</jnl>.
- <lit67><jnl>S. Lanzalaco, A. Galia, F. Lazzano, R.[^]R. Mauro, O. Scialdone, *J. Polym. Sci. Part A* **2015**, *53*, 2524--2536</jnl>.
- <lit68><jnl>D. O'Hagan, *Chem. Soc. Rev.* **2008**, *37*, 308--319</jnl>.
- <lit69><jnl>H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119--2183</jnl>.

<lit70><jnl>S. Lanzalaco, M. Fantin, O. Scialdone, A. Galia, A.[^]A. Isse, A. Gennaro, K. Matyjaszewski, *Macromolecules* **2017**, *50*, 192--202</jnl>.

<lit71><jnl>B. Ameduri, *Chem. Rev.* **2009**, *109*, 6632--6686</jnl>.

<lit72><jnl>Y. Wang, H. Wang, K. Liu, T. Wang, C. Yuan, H. Yang, *RSC Adv.* **2021**, *11*, 30734</jnl>.

<lit73><jnl>Y. Wu, Y. Zhou, J. Zhu, W. Zhang, X. Pan, Z. Zhang, X. Zhu, *Polym. Chem.* **2014**, *5*, 5546--5550</jnl>.

<lit74><jnl>M. Guerre, B Améduri, V Ladmiral, *Polym. Chem.* **2016**,*7*, 441--450</jnl>.

<lit75><jnl>A. Taguet, B. Améduri, B. Boutevin, *Adv. Polym. Sci.* **2005**, *184*, 127--211</jnl>.

<lit76><jnl>M. Guerre, J. Schmidt, Y. Talmon, B. Améduri, V.Ladmiral, *Polym. Chem.* **2017**,*8*, 1125--1128</jnl>.

<lit77><jnl>K. Kallitsis, T. Soulestin, S. Tencé-Girault, C. Brochon, É. Cloutet, F. Domingues[^]dos[^]Santos, G.[^]P. Hadziioannou, *Macromolecules* **2019**, *52*, 8503--8513</jnl>.

<lit78><jnl>K. Feng, B. Tang, P. Wu, *J. Mater. Chem. A* **2015**, *3*, 12609--12615</jnl>.

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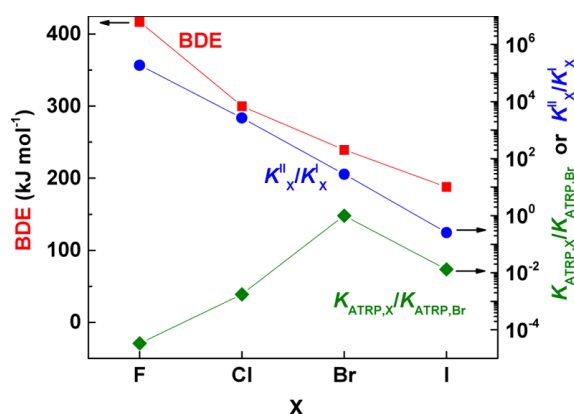


Figure 1 Bond dissociation energy, K_X^{II}/K_X^I ratio of $X<C->Cu/TPMA$ complexes, and $K_{ATRP,X}/K_{ATRP,Br}$ for the reaction between $[Cu^I TPMA]^+$ and BnX ($X=F, Cl, Br, I$) at $25^\circ C$. Reproduced with permission from ref. [70] Copyright (2017), American Chemical Society.

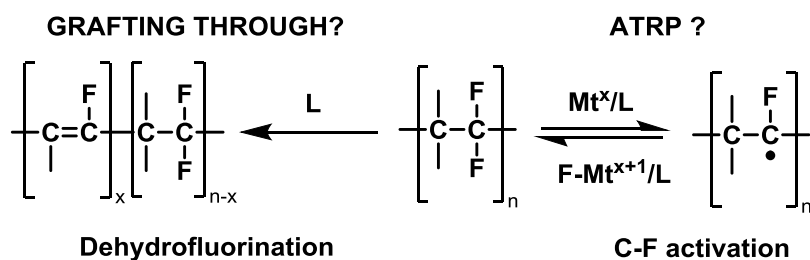


Figure 2 Grafting of fluoropolymers via ATRP: C<C->F activation or dehydrofluorination.