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Mild-Temperature $Mn_2(CO)_{10}$-Photomediated Controlled Radical Polymerization of Vinylidene Fluoride and Synthesis of Well-Defined Poly(vinylidene fluoride) Block Copolymers

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Supporting Information

ABSTRACT: By contrast to typical high-temperature (100−250 °C) telo-/polymerizations of gaseous fluorinated monomers, carried out in high-pressure metal reactors, the visible light, $Mn_2(CO)_{10}$-photomediated initiation of vinylidene fluoride (bp = −83 °C) polymerization occurs readily from a variety of alkyl, semifluorinated, and perfluorinated halides at 40 °C, in low-pressure glass tubes and in a variety of solvents, including water and alkyl carbonates. Perfluorinated alkyl iodide initiators also induce a controlled radical polymerization via iodine degenerative transfer (IDT). While IDT proceeds with accumulation of the less reactive P_m-CF_2-CH_2-I vs the P_n-CH_2-CF_2-I chain ends, $Mn_2(CO)_{10}$ enables their subsequent quantitative activation toward the synthesis of well-defined poly(vinylidene fluoride) block copolymers with a variety of other monomers.

Fluorinated (co)polymers are fundamental specialty materials with a wide range of high-end applications[1] requiring their precise synthesis. However, while novel controlled radical polymerization (CRP) methods[2] (atom transfer, nitroxide, or addition−fragmentation) have recently seen remarkable developments[2,3] and have proven very effective for (meth)acrylates or styrene, their applicability in the CRP of main-chain fluorinated alkene monomers (FMs: vinylidene fluoride (VDF), hexafluoropropene (HFP), tetrafluoroethylene, etc.) still awaits demonstration.

The most successful approach to FM-CRP[1] has emerged from high-temperature (100−250 °C) free radical VDF telomerizations[4] with polyhalides,[1a−c] especially (per)-fluorinated iodine chain-transfer (CT) agents,[5−9] and is mechanistically based on one of the oldest CRP methods,[10] the iodine degenerative transfer[3,11] (IDT: $P_n^{\bullet} + P_m\text{-I} \rightleftharpoons P_n\text{-I} + P_m^{\bullet}$).[1,5]

However, IDT always requires a free radical source (e.g., *tert*-butyl peroxide),[1,4,5,7] as *direct* metal-catalyzed initiation from perfluoroalkyl iodides (R_F-I) or any other halides is not available. Indeed, while such electrophilic $R_F^{\bullet}$ radicals add readily to alkenes using Cu, Pd, or Ti catalysts,[12] their addition to electrophilic, fluorinated substrates (FMs) at $T < 100$ °C, and especially at room temperature (rt), is lacking. Conversely, while VDF polymerization can be initiated at rt,[13] only very low VDF oligomers (DP = 1−3) may be obtained, even at $T > 100$ °C from transition metal salts and polyhalides,[1,5,14] and there are no reports on metal-mediated FM/VDF polymerizations, let alone VDF-CRP. Moreover, by contrast to the CRP of acrylates or styrene, VDF-IDT produces *two* halide chain ends, P_n-CH_2-CF_2-I and P_m-CF_2-CH_2-I, with widely different reactivity.[8]

Thus, the ability to initiate *directly* from halides, mediate rt FM-CRP, and activate *both* PVDF-I termini would be of great value in the controlled synthesis of well-defined block, graft, and star FM structures, which, due to the current lack of such chemistry, inevitably end up as mixtures of homo- and copolymers.

Consequently, the study of FM-CRPs and the synthesis of complex architectures thereby derived is a worthy[1,5−8] yet very challenging endeavor, especially on a laboratory scale, as VDF boils at −83 °C, and typical telo-/polymerizations are carried out at 100−250 °C.[1] Accordingly, while styrene or acrylate CRPs can easily be sampled on a 1 g scale, kinetics of VDF polymerizations involve many time-consuming one-data-point experiments in expensive high-pressure metal reactors, which require at least tens of grams of monomer. Thus, development of methods allowing polymerizations to proceed at mild temperatures in inexpensive pressure glass tubes would be highly desirable, as such methods could be easily adapted for fast catalyst and reaction condition screening and take advantage of photochemistry.

As such, while VDF telomerizations under high-power UV are available,[1,5,15] there are no reports on VDF polymerizations under regular *visible* light. To this end, we decided to investigate mild photochemical means of radical generation,[16] such as transition-metal-mediated photopolymerizations using low wattage (<30 W), spiral, compact white light fluorescent bulbs.

Since VDF is a very reactive monomer, effective rt initiators should provide highly reactive radicals. Conversely, the visible-light-generated metalloradical should be a very good halide abstractor. Prototypical examples[16] are $(CO)_n$Mt-Mt$(CO)_n$-type dimers, where the inexpensive $Mn_2(CO)_{10}$[17a] is the most popular.[16] The Mn−Mn linkage is weak (20−40 kcal/mol),[16,17b] and rt visible light photolysis provides the $Mn(CO)_5^{\bullet}$ $17e^-$ metalloradical with good quantum efficiency.[18]

$Mn(CO)_5^{\bullet}$ cleanly abstracts halides from a variety of substrates,[16c] reacting faster with primary rather than secondary

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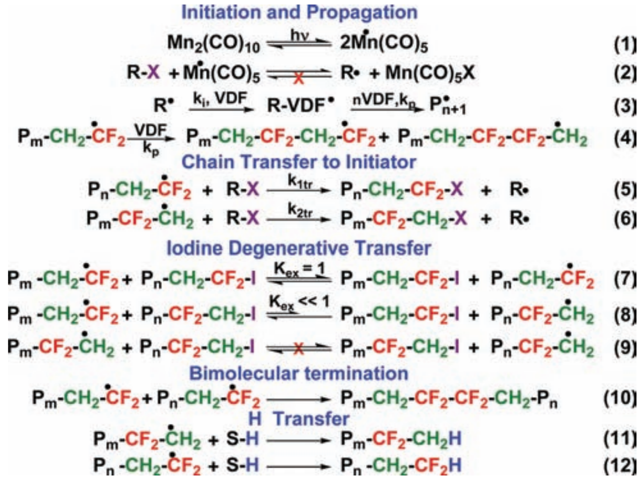
or tertiary ones, yet there are no examples with semi- or perfluoroalkyl substrates. Moreover, while $Mn_2(CO)_{10}/CCl_4$-initiated polymerizations were developed in the 1960s,[19] $Mn_2(CO)_{10}$ was only recently employed in other free radical polymerizations (FRP),[20] and especially in the photomediated IDT of vinyl acetate (VAc) and its copolymers,[21] where $Mn(CO)_5^\bullet$ activates an alkyl iodide initiator, but the resulting $Mn(CO)_5$-I is not involved in the reversible I transfer. We thus decided to assess its scope and limitations for FM-CRPs and optimize the system.

While visible light could also be invoked in the photodissociation of RX, control experiments (Table S1, exp. 1−4) revealed no polymerization in the dark, or with illumination in the absence of $Mn_2(CO)_{10}$. Though polymerizations could easily be carried out anywhere from $T = 0$ to 100 °C, (Table S1, exp. 6−12), we selected $T = 40$ °C for all further experiments as a good compromise between rate, minimization of possible higher temperature side reactions, and a safe pressure inside the tube. In fact, simply lowering the bottom part of the light bulb inside the oil bath (Figure S1) helped maintain such temperature, with minimal additional heating from the hotplate.

Typical VDF reactions are carried out in the non-solvent acetonitrile (ACN),[1,4−8] but there is very little data[22] on the solvent effect in VDF polymerizations, let alone photopolymerizations. Thus, we first surveyed a large number of solvents (Table S2), noting that minimization of solvent CT outweighs solubility considerations. Indeed, all good PVDF solvents[23a] (DMF, DMAC, etc.) acted as strong CT agents and led to very low conversions. By contrast, while fast polymerizations could be carried out even in water, remarkable trends were observed with carbonates, especially dimethyl carbonate (DMC), a green solvent.[23b] Indeed, although DMC does not dissolve PVDF at rt, and similarly to that with ACN, the reaction displays typical features of heterogeneous polymerizations of gaseous monomers,[23c] it provides by far the fastest reaction rates, at least 5 times those obtained in ACN. As DMC is stable to photolysis,[24] this is not a photosensitizing effect, but a consequence of low CT, better monomer solubilization, and polymer swelling,[25] which enables faster monomer diffusion to the propagating center.

The proposed reaction mechanism is outlined in Scheme 1, and the polymerization setup is illustrated in Figure S1. Following photolysis of $Mn_2(CO)_{10}$ (eq 1), irreversible[21] halide abstraction from R-X (driven by the formation of high bond dissociation energy (BDE) Mn-X, X = Cl, Br, I, eq 2)[26] affords $Mn(CO)_5$-X and $R^\bullet$, which, if reactive enough, initiates VDF polymerization (eq 3). As VDF is asymmetrical, both 1,2- and 2,1-modes of propagation (eq 4, head-to-tail, HT, ~95%,[1,6,22] and respectively head-to-head, HH) are possible in FRPs.

Scheme 1. $Mn_2(CO)_{10}$-Photomediated VDF-CRP



Out of all halides investigated (Chart S1, Table S1), most of which were *never previously reported in conjunction with $Mn_2(CO)_{10}$*, reactive alkyl polyhalides, as well as semi- and perfluorinated halides such as $CHCl_3$, CCl_4, CCl_3-Br, CCl_3-CCl_3, $CF_3(CF_2)_2CO$-Cl, CF_3-SO_2-Cl, Cl-CF_2-CClF-Cl, Cl-$(CF_2)_8$-Cl, -$(CF_2$-$CFCl)_n$-, EtOOC-CF_2-Br, Br-CF_2-CH_2-CF_2-Br, Br-$(CF_2)_4$-Br, CH_3-I, $CH_3(CH_2)_5$-I, I-$(CH_2)_{10}$-I, C_6F_5-CF_2-I, H-CF_2-CF_2-CH_2-I, EtOOC-CF_2-I, Cl-CF_2-CFCl-I, CF_3-I, CF_3CF_2-I, $(CF_3)_2CF$-I, $(CF_3)_3C$-I, $CF_3(CF_2)_3$-I, and I-$(CF_2)_{4,6}$-I, all led to polymer formation, as demonstrated (NMR) in Figure S2 and Table S3. Remarkably, initiation is afforded not only from polyhalides and all R_F-I structures (which also provide VDF-IDT *vide infra* and dramatic reduction of HH defects, Figure S2b) but also from semifluorinated chain end models, and especially from simple inactivated alkyl iodides, thus indicating the feasibility of initiating block or graft VDF copolymerization *directly* from the corresponding initiators anchored on polymeric chains, surfaces, etc. Initiation is demonstrated not only for VDF but also for $CF_2{=}CFCl$, $CF_2{=}CCl_2$, $CF_2{=}CFBr$, $CH_2{=}CFH$, and VDF random copolymers with $CF_2{=}CF(CF_3)$ and $CF_2{=}CF(OCF_3)$ (Table S1).

Subsequently, the polymerization outcome is controlled by the carbon−halide bond strength, which determines the RX CT ability (eqs 5 and 6). Accordingly, the initiators fall into three classes which require different amounts of $Mn_2(CO)_{10}$ for activation, and VDF undergoes conventional FRP for RX (X = Cl, Br, I) and IDT-mediated CRP for R_F-I.

Thus, initiators with strong R-X bonds (alkyl iodides, $CHCl_3$, R_F-Cl) do not undergo noticeable CT with $PVDF^\bullet$, demand stoichiometric $Mn_2(CO)_{10}$ activation, and afford PVDF with no halide chain ends (Figure S2). By contrast, substrates with weak R-X bonds (e.g., CF_3SO_2-Cl, C_2Cl_6, CCl_4, CCl_3Br, R_F-X, X = Br, I) *do undergo* CT to the initiator (eqs 5 and 6), require reduced (10%) amounts of $Mn_2(CO)_{10}$, and afford halide-functionalized PVDF-X (X = Cl, Br, I, Figure S2). However, while good Cl and Br CT agents can at best provide efficient telomerizations,[4] uncatalyzed halide DT-CRP occurs only for iodine. As such, high-CT R_F-I initiators suitable for IDT-CRPs[5] are converted early in the process into macromolecular PVDF-I CT agents,[8] where the terminal P_m-CF_2-CH_2-I^{5-9} 2,1-unit is about 25 times less reactive toward IDT than the isomeric P_n-CH_2-CF_2-I 1,2-unit.[8]

Once all the R_F-I initiator is consumed via CT, no new PVDF-I chains are generated, and the thermodynamically neutral, *reversible* I exchange (IDT, $K_{equil} = 1$) between equally reactive, propagating and dormant P_n-CH_2-$CF_2^\bullet$ and P_m-CH_2-CF_2-I terminal 1,2-units (eq 7) is in operation. This enables IDT-CRP, as demonstrated (Figures 1 and S3, VDF; Figure S4, VDF-*co*-HFP) by the linear dependence of M_n on conversion and moderate polydispersity index (PDI) values, which indicate that $Mn_2(CO)_{10}$ supports a photo-CRP over a wide range of molecular weights (M_n = 1000−25 000). However, such CRP toward higher M_n values is kinetically impractical under these conditions.

While IDT catalysis would lead to a PDI decrease,[3,11] control experiments (Figure S5) reveal that, consistent with PVAc-

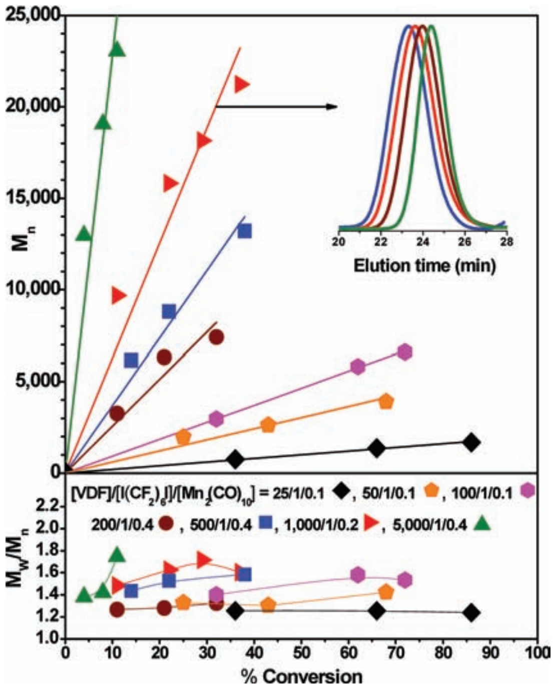


Figure 1. Dependence of M_n and M_w/M_n on conversion in $Mn_2(CO)_{10}$-photomediated VDF-IDT. Inset: GPC traces for $[VDF]/[I(CF_2)_6I]/[Mn_2(CO)_{10}]$ = 1000/1/0.2 trace.

IDT,[21] the photochemically inactive[27a] $Mn(CO)_5$-I is incapable of reversibly transferring I. Conversely, although R_F-$Mn(CO)_5$ (R_F = CH_2F, CF_2H)[27b] are known, organometallic CRP mediation by PVDF-$Mn(CO)_5$ can be discounted on the basis of the observed -I, not -H or -$Mn(CO)_5$ chain ends, of the successful CRP with *catalytic*, not stoichiometric $Mn_2(CO)_{10}$ vs R_F-I, and considering the BDE order (R_F-$Mn(CO)_5$ < $(CO)_5$Mn-$Mn(CO)_5$ < R_F-I < I-$Mn(CO)_5$, i.e., 34,[27b] 38,[26b] 48,[28] and 54 kcal/mol[26]), consistent with the instability of Mn alkyls under irradiation.[26b]

In IDT, HH defects are dramatically suppressed (Figure S2), being intercepted as P_m-CF_2-CH_2-I. I-R_F-I initiators are particularly suitable for FM-CRPs, as bidirectional growth from difunctional propagating species,[10] in conjunction with initiator or chain-end halide activation by the continuously photogenerated $Mn(CO)_5^{\bullet}$ [18b] (eq 2), compensates for termination by radical coupling[10] and maintains a steady-state radical concentration.

However, due to the much stronger -CH_2-I bond, the cross-IDT between the 1,2- and 2,1- units (eq 8) is shifted toward the irreversible buildup of P_n-CF_2-CH_2-I chain ends, whereas the IDT of the 2,1-terminal units is virtually non-existent (eq 9).[7,8]

Although these are unavoidable features in conventional IDT as well,[7,8] while the concentration of active -CH_2-CF_2-I termini decreases and unreactive -CF_2-CH_2-I species accumulate with conversion (Figure S6) and contribute to PDI broadening,[8,9,21] the *total* (-CH_2-CF_2-I + -CF_2-CH_2-I) iodine functionality remains at least 95%, even at larger levels of $Mn_2(CO)_{10}$, which is quite adequate for block copolymer synthesis, on the condition that *both* halide chain ends can be activated.

Yet, while high-temperature ethylenation,[29] azidation,[29c] and block copolymer synthesis via ATRP[29d] or IDT[9] were previously attempted from PVDF-I, all such endeavors were fundamentally incomplete, due to the failure of the respective chemistries to activate the stronger and dominant -CF_2-CH_2-I termini. Thus, the products were always inseparable, ill-defined mixtures.

By contrast, $Mn(CO)_5^{\bullet}$ affords the clean and quantitative activation of *both* -CH_2-CF_2-I and -CF_2-CH_2-I chain ends and enables the synthesis of well-defined block copolymers. Selected examples of the associated ^1H NMR characterization are presented in Figure 2 and Table S4. In addition to acetone and water (δ = 2.05 and 2.84 ppm),[30] the HT -CF_2-[CH_2-CF_2]$_n$-CH_2- (**a**) and HH -CF_2-CH_2-CH_2-CF_2- (**a′**) PVDF linkages[29,31] are observed at δ = 2.8−3.1 and 2.3−2.4 ppm, respectively. Resonance **b** (δ = 3.25 ppm) confirms the R_F-CH_2-CF_2- connectivity with the first polymer unit, and the 1,2-CH_2-CF_2-I (**c**) and 2,1-CF_2-CH_2-I (**c′**) iodine chain ends are seen[7] at δ = 3.62 and 3.87 ppm (Figure 2a).

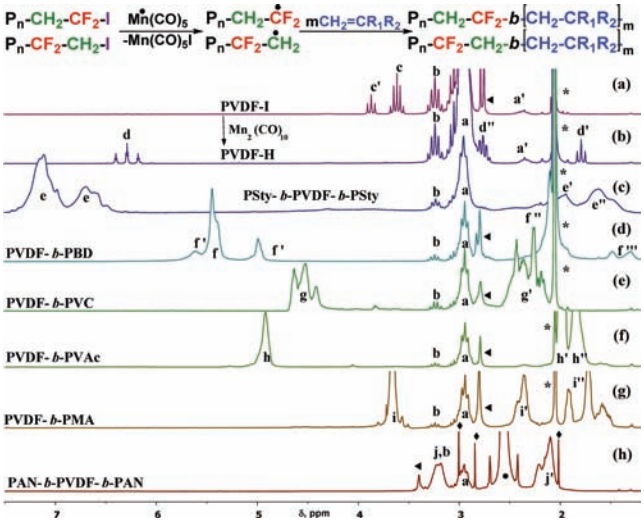


Figure 2. 500 MHz ^1H NMR spectra of PVDF-I, PVDF-H, and various PVDF block copolymers. All in d_6-acetone, except PAN in d_6-DMSO. ◀ = H_2O, * = acetone, ♦ = DMAC, ● = DMSO.

While VDF-FRP terminates primarily by recombination of 1,2-units (eq 10),[1,4−9] in VDF-IDT, trace termination by H transfer to the propagating chains (eqs 11 and 12, i.e., -CH_2-CF_2-*H* and -CF_2-CH_3, peaks **d**, **d′**) is seen at δ = 6.30 and 1.80 ppm.[31c] Upon treatment of PVDF-I with stoichiometric $Mn(CO)_5^{\bullet}$, complete activation of *both* halide chain ends occurs. Thus, in the absence of a monomer as addition substrate, the resulting radicals are deactivated by H abstraction from solvent to generate the same **d** and **d′** peaks and a more resolved -CH_2-CF_2-*CH_2*-CF_2-H **d″**, δ = 2.77 ppm[31e] (Figures 2b and S2d,e, ^{19}F NMR).

As such, carrying out the reaction in the presence of a radically polymerizable alkene leads to the first examples of well-defined, AB- or ABA-type PVDF block copolymers with styrene (**e**, **e′**), butadiene (**f**, **f′**, **f″**, **f‴**), vinyl chloride (**g**, **g′**), vinyl acetate (**h**, **h′**, **h″**), methyl acrylate (**i**, **i′**, **i″**), and acrylonitrile (**j**, **j′**), initiated from *both* PVDF halide chain ends (Table S4 and Figure 2c−h). While here $Mn_2(CO)_{10}$ operates simply as a photoactivator and there is no IDT, control of the block copolymerization by other CRP methods can be envisioned.

To summarize, we have demonstrated for the first time, using VDF as a model for main-chain fluorinated gaseous monomers, that the initiation of the polymerization can easily be accomplished at mild temperatures, *directly* from a variety of alkyl, semifluoroalkyl, and perfluoroalkyl halides (Cl, Br, I) using a visible light, $Mn_2(CO)_{10}$-photomediated protocol, carried out in low-pressure glass tubes, and which is especially successful in DMC. Moreover, in the presence of perfluorinated alkyl iodides, such reactions follow an IDT mechanism, leading to a CRP process. Finally, the $Mn_2(CO)_{10}$-induced complete activation of *both* $-CH_2-CF_2-I$ and $-CF_2-CH_2-I$ halide chain ends affords the first examples of well-defined block copolymers initiated from PVDF-I. The direct halide VDF initiation, VDF-CRP, and the complete halide chain-end activations open up novel synthetic avenues for the photomediated synthesis of architecturally complex fluoromaterials. Thus, main-chain fluorinated polymers can be grafted or block copolymerized directly from any substrates containing suitable halide initiators, and conversely, the polymerization of other monomers can be initiated quantitatively from their chain ends. Using multifunctional initiators, the synthesis of star and hyperbranched systems can be envisioned as well. Lastly, the R_F-I/$Mn_2(CO)_{10}$ protocol may also be applicable in radical trifluoromethylation reactions, which are in great demand in organic chemistry.[32]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, techniques, experimental procedures, initiator chart, ^{1}H and ^{19}F NMR and IR spectra and discussions, tables with full characterization of all homo- and copolymerizations (including initiator and solvent effect), kinetics, and dependence of the iodine chain ends on conversion. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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