Atom Transfer Radical Polymerization Initiated with Vinylidene Fluoride Telomers

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Poly(vinylidene fluoride) (PVDF) is an important engineering polymer whose remarkable piezoelectrical properties and weatherability gave rise to a broad range of applications. Because it is an expensive material, attention has been paid in the past to its ability to be blended with other polymers, mostly by means of PMMA-based block copolymers used as compatibilizers.[1,2] Although block copolymers can now be synthesized by controlled radical polymerization (CRP),[3,4] the preparation of well-defined PVDF-based block copolymers is still an important challenge. Nevertheless, many studies have controlled PVDF chain-end structures using functional transfer agents by *telomerization* methods.[5] Recently, we reported the peroxide-induced telomerization of VDF with chloroform as a telogen agent to produce well-defined trichloromethyl-terminated VDF telomers $CCl_3(C_2H_2F_2)_nH$.[6]

Atom transfer radical polymerization (ATRP)[3] is one of the most versatile methods for synthesizing homopolymers and copolymers with predetermined molecular weights and narrow molecular weight distributions. It is based on the combination of an organic halide initiator (RX) with a metal/ligand catalytic system which is able to promote fast initiation compared to propagation and then reversibly activate halogenated chain ends (P_nX) during polymerization.

1,1,1-Trichloroalkanes, CCl_3R, are efficient initiators for ATRP of styrene (St),[7] methyl methacrylate (MMA),[8] and acrylates[8] catalyzed by the CuCl/2,2′-bipyridine system (Cu/bpy). The nature of the R group has little influence on the molecular weight and polydispersity of the resulting polymers.[7,8] On the other hand, it affects the rates of polymerization through both the initiator's functionality and the concentration of deactivator (Cu(II)) in the system.[7,8] When R is an electron-withdrawing group (CO_2CH_3, Cl), CCl_3R acts as a multifunctional initiator for both styrene[7] and MMA.[8] CCl_3-terminated vinyl acetate telomers[9] and a poly(*n*-butyl acrylate) initiated with a CCl_3-terminated azo initiator[10] were also successfully used as macroinitiators for ATRP of styrene to synthesize block copolymers.

Very recently, the combination of telomerization and ATRP was used for the synthesis of PSt-*b*-PVDF-*b*-PSt block copolymers starting from a $BrCF_2$-terminated VDF difunctional telomer.[11] However, the reaction times were very long (several days), molecular weights were uncontrolled, and the polydispersities were large. In this

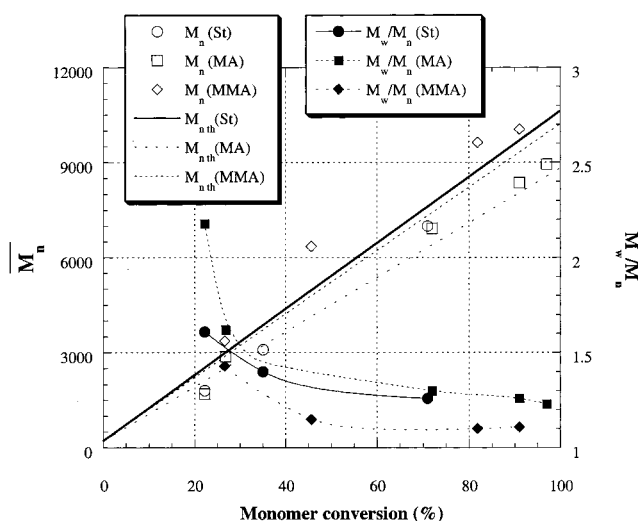† Current address: Rhodia, Centre de Recherches d'Aubervilliers, 52 rue de la Haie Coq, 93308 Aubervilliers, France.

Figure 1. Evolution of M_n and M_w/M_n with monomer conversion in ATRP of styrene, MMA, and MA initiated by T^1 and catalyzed by CuCl/Bpy. T^1/CuCl/Bpy/monomer = 1/0.5/1/100 for MMA (50 vol % 1,2-dimethoxybenzene, $T = 90$ °C), MA (10 wt % 1,2-dimethoxybenzene, $T = 90$ °C), and St (10 wt % 1,2-dimethoxybenzene, $T = 130$ °C).
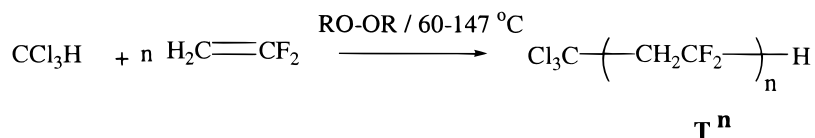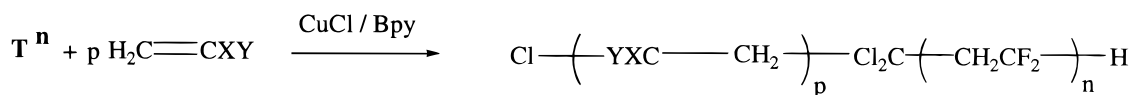
communication, we report the use of α-trichloromethylated VDF telomers as new ATRP initiators for synthesizing PVDF-based block copolymers according to the two-step procedure described in Scheme 1.

The telomerization of VDF with chloroform has been studied in detail.[6,12] The initial chloroform to VDF molar ratio was varied at different temperatures, and the resulting telomers T^n (*n* represents the number-average degree of polymerization calculated from ^{1}H NMR) were characterized by GC and ^{1}H, ^{13}C, and ^{19}F NMR (Table 1). NMR confirmed that the telomer structures were mainly controlled by a hydrogen atom transfer from chloroform to the vinylidene fluoride radical.[12]

The VDF/chloroform 1:1 adduct (1,1,1-trichloro-2,2-difluoropropane, $CCl_3CH_2CF_2H$) is an appropriate model compound to study the ability of higher molecular weight VDF telomers to initiate ATRP efficiently. Because of the relatively low transfer constant to chloroform in VDF polymerization ($C_{tr}^\infty = 0.06$ at 141 °C),[6] a 15-fold excess of chloroform relative to VDF was necessary to obtain a low molecular weight telomer distribution with a sufficient amount of the 1:1 adduct ($DP_n = 2.05$, based on NMR). The purest distillation fraction was contaminated with 17% of the diadduct. An alternative approach was to consider the CCl_4/VDF 1:1 adduct $CCl_3CH_2CF_2Cl$ [13] (T^1) as a model initiator. In Cu-catalyzed redox telomerization, radical generation from the trichloromethyl end of T^1 is highly favored compared with that of the CF_2Cl end.[13] This means that the latter end should generate little or no radicals when T^1 is used to initiate ATRP. Figure 1 shows the evolution of molecular weights and polydispersities with monomer conversion for ATRP of styrene, MMA, and MA initiated by T^1 and catalyzed by CuCl/bpy.[14] M_n increased linearly with conversion for all monomers, and values were very close to those predicted, assuming quantitative initiation and no transfer ($M_{n,th} = ([M]_0/[T^1]_0) \times$ (monomer conversion) + $(MW)_{T^1}$). Polydispersities were low at high monomer conversion ($1.1 < M_w/M_n < 1.3$).

Scheme 1

First step: Radical Telomerization of VDF with Chloroform

$$CCl_3H \quad + \ n\ H_2C\!\!=\!\!CF_2 \quad \xrightarrow{\text{RO-OR / 60-147 °C}} \quad Cl_3C\!\!-\!\!\left(\!CH_2CF_2\!\right)_{\!n}\!\!-\!\!H$$

$$\mathbf{T}^{\,\mathbf{n}}$$

Second step: ATRP of H₂C=CXY (Sty, MMA or Acrylate) Initiated by **Tⁿ** and Catalyzed by CuCl / Bpy

$$\mathbf{T}^{\,\mathbf{n}} + \ p\ H_2C\!\!=\!\!CXY \quad \xrightarrow{\text{CuCl / Bpy}} \quad Cl\!-\!\left(\!YXC\!-\!CH_2\!\right)_{\!p}\!Cl_2C\!-\!\left(\!CH_2CF_2\!\right)_{\!n}\!\!-\!\!H$$

PVDF-b-PS

PDVF-b-PMMA

PVDF-b-PAcrylate

Table 1. Synthesis and Characterization of CCl₃-Terminated VDF Telomers (Tⁿ)

Tⁿ a	$[CCl_3H]_0/[VDF]_0$	catalyst	T (°C)	t (h)	$[CuCl]_0/[VDF]_0$	VDF conv (%)	purification
T¹	1	CuCl/CuCl₂	145	8	2×10^{-2}	38	distillation
T⁵	5	DTBP[b]	147	5	10^{-2}	87	distillation fraction
T¹¹	5	DTBP	147	5	10^{-2}	87	distillation residue, precipitated[d]
T¹⁶	1.2	DTBCP[c]	60	7	10^{-2}	55	precipitation[d]

[a] Tⁿ stands for CCl₃(C₂H₂F₂)ₙH telomers, except T¹ (CCl₃CH₂CF₂Cl). *n* represents the related number-average degree of polymerization determined by ¹H NMR; all the reactions were carried out in acetonitrile. [b] Di-*tert*-butyl peroxide. [c] Di-(4-*tert*-butylcyclohexyl) peroxidicarbonate. [d] In hexane.

Table 2. ATRP Initiated by VDF Telomers; M_n and M_w/M_n vs Conversion Relationship (Tⁿ/CuCl/Bpy = 1/0.5/1 for All Monomers)

entry	monomer	$[M]_0$ (M)	solvent	temp (°C)	VDF telomer ($10^2 \times$ concn (M))	time (h)	$M_{n,th}$ [a]	M_n [b]	M_w/M_n	conversion (%)
1	MMA	4.7	DMB[c]	90	T¹ (4.70)	2	8520	9620	1.10	85.1
2	MMA	4.7	acetone	90	T⁵ (4.70)	1	2430	3065	1.18	19.6
3	MMA	4.7	acetone	90	T⁵ (4.70)	16.5	9470	10210	1.13	90.0
4	MMA	4.7	acetone	90	T¹¹ (4.70)	1.75	4420	6200	1.13	37.0
5	MMA	4.7	acetone	90	T¹¹ (4.70)	17	9520	9740	1.12	89.1
6	MMA	4.7	acetone	90	T¹⁶ (4.70)	3.33	7540	8290	1.15	64.0
7	Sty	7.98	DMB	130	T¹ (7.98)	9.66	7610	7000	1.27	71.0
8	Sty	4.35	DPE[d]	130	T¹¹ (4.35)	0.5	2470	2110	1.27	16.0
9	Sty	4.35	DPE	130	T¹¹(4.35)	15.75	8705	7950	1.22	75.8
10	BA	3.49	acetone	90	T⁵ (3.49)	1	1910	1140	1.21	11.3
11	BA	3.49	acetone	90	T⁵ (3.49)	17	2110	1900	1.25	13.9
12	BA	3.49	acetone	90	T⁵ (3.49)	140	3700	4440	1.19	25.7
13	BA[e]	3.49	acetone	90	T⁵ (3.49)	140	9590	10600	1.30	73.1
14	MA	10.2	DMB	90	T¹(10.2)	42.25	8050	8360	1.26	91.0

[a] $M_{n,th} = ([M]_0/[T^n]_0) \times$ (monomer conversion) + $(MW)_{T^n}$. [b] Measured by GPC: THF eluent for samples initiated with T¹, DMF eluent otherwise; PMMA standards for MMA, PS standards for St, MA, and BA. [c] 1,2-Dimethoxybenzene. [d] Diphenyl ether. [e] Addition of 6 weight equivalents of Cu(0) turnings compared to CuCl.

We also initiated ATRP of St, MMA, MA, and *n*-butyl acrylate (BA) with VDF telomers of varying DP_n values equal to 5, 11, and 16. Solvents were selected that provided a good compromise between a high proportion of catalyst solubilized in the reaction medium, acceptable rates of polymerization, and good control over both M_n and M_w/M_n: diphenyl ether for styrene, acetone for MMA, n-BA, and MA (50 vol % in all cases). Table 2 shows M_n increased from that of the VDF telomer during polymerization and was close to the theoretical value for all of the Tⁿ/monomer pairs. Starting from VDF telomers fractionated by distillation or precipitation (Figure 2), the polydispersities remained consistently low during the polymerization (typically M_w/M_n < 1.2 at high monomer conversion). Moreover, no residual trace of the starting PVDF could be detected by GPC using DMF as the eluent when superimposing

the initial VDF telomer (T¹¹) and the derived block copolymer traces, *for all of the monomers polymerized* (Figure 2). This strongly supports the formation of pure block structures. As shown in Figure 2, the refractive index increment of PVDF in DMF is negative (−0.023 mL g⁻¹ at λ = 546 nm),[15] whereas those for St and MMA are positive (equal to 0.16[16] and 0.06 mL g⁻¹,[16] respectively).

In the case of the acrylates (MA and BA), polymerization was very slow. For example, ATRP of BA reached about 25% conversion after 140 h. This slow polymerization can be explained by the initial production of a higher Cu(II) concentration than when alkyl halides are used as initiators due to faster initiation.[8] ESR studies showed that less Cu(II) is usually present during polymerization of acrylates than in that of MMA[17] or styrene.[18] Therefore, the acrylate-based systems are
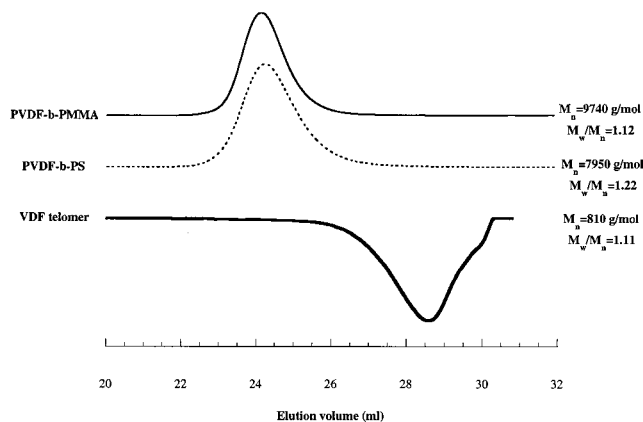
Figure 2. GPC traces of T^{11} (a) and corresponding block copolymers with (b) St (Table 2, entry 5) and (c) MMA (Table 2, entry 9).

more sensitive to Cu(II), which explains the dramatic decrease of rates observed for RCCl$_3$ initiators. To prevent this drawback, Cu(0) metal turnings were added in the case of BA (Table 2, entry 13) to remove the excess of Cu(II).[19] This resulted in a considerable increase of the polymerization rate while maintaining good control over molecular weights and polydispersities.

In summary, vinylidene fluoride telomers have been synthesized and used to initiate ATRP of St, MMA, MA, and BA. A dual method comprising the telomerization of VDF with chloroform followed by ATRP initiated from the resulting $CCl_3(C_2H_2F_2)_nH$ telomers has been successfully developed. CCl_3-terminated VDF telomers promote fast initiation relative to propagation in ATRP of St, MMA, and acrylates. By varying $[CCl_3H]_0/[VDF]_0$ and $[M]_0/[T^n]_0$ ratios in the telomerization and ATRP steps, respectively, the chain length of both blocks and copolymer composition are easily predetermined. Further studies on the synthesis of VDF telomers with higher DP$_n$ and their use to initiate ATRP are in progress.

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(12) A typical example of the telomerization of vinylidene fluoride with chloroform is as follows: a 1 l Hastelloy autoclave was charged with chloroform (1.5 mol, 161.3 g), (4-*tert*-butylcyclohexyl) peroxidicarbonate (12.5 mmol, 4.97 g), and 200 g of acetonitrile. After cooling and degassing the reactor, vinylidene fluoride (1.25 mol, 80.0 g) was introduced. The reactor was then heated to 60 °C, and the reaction was run for 7 h. The autoclave was then cooled to 0 °C, and the unreacted VDF was released. After evaporation of the remaining volatiles, the crude solid product was dissolved into acetone and precipitated from hexane. A white powder was recovered and dried under vacuum (M_n = 1145). ^{1}H NMR (200 MHz, d_6-acetone, δ, ppm): 1.70 (t, $^3J_{HF}$ = 14.6 Hz, $-CF_2CH_3$), 2.28 (broad t, $^3J_{HH}$ = 6.9 Hz, $-CF_2CH_2CH_2$-CF$_2$−), 2.85 (q, $^3J_{HF}$ = 15.1 Hz, $-CF_2CH_2CF_2$−), 3.65 (t, $^3J_{HF}$ = 14.8 Hz, CCl$_3$CH_2CF$_2$−), 6.20 (tt, $^2J_{HF}$ = 57.2 Hz, $^3J_{HF}$ = 5.2 Hz, $-CF_2H$). ^{13}C NMR (200 MHz, d_7-DMF, δ, ppm): 27.70 (t, $^2J_{CF}$ = 4.8 Hz, $-CF_2CH_3$), 43.84 (q, $^2J_{CF}$ = 24.2 Hz, $-CF_2CH_2CF_2$−), 79.20 (s, Cl$_3$C−), 120.84 (t, $^1J_{CF}$ = 245.5 Hz, $-CF_2$−). ^{19}F NMR (200 MHz, d_6-acetone, δ, ppm): −91 (m, $-CH_2CF_2CH_2$−), −94.5 (m, CCl$_3$CH$_2$CF_2−), −107.4 (m, $-CF_2CH_3$), −113.5 and −116.2 (2m, $-CH_2CF_2CF_2CH_2$−), −114.8 (dm, $^2J_{HF}$ = 57.6 Hz, $-CF_2H$).
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(14) A typical example of an ATRP procedure is as follows (entry 7 of Table 2): CuCl (0.11 mmol, 11.5 mg), 2,2′-dipyridyl (0.23 mmol, 36.3 mg), degassed styrene (23.2 mmol, 2.42 g), 0.24 g of 1,2-dimethoxybenzene, and T^1 (0.232 mmol, 50.6 mg) were introduced into a degassed glass tube equipped with a magnetic stirrer. The tube was frozen in liquid nitrogen and degassed by three pump−freeze−thaw cycles. It was sealed under vacuum and placed in an oil bath at 130 °C. After 9 h 40 min, the tube was opened, and the reaction mixture was passed through an alumina column to remove copper. Conversion: 71% (GC); M_n = 7000 g/mol (GPC in THF), M_w/M_n = 1.27.
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