Synthesis of Block Copolymers Possessing Fluoropolymer and Non-Fluoropolymer Segments by Radical Polymerization

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ABSTRACT: The synthesis of block copolymers comprising fluoropolymer and non-fluoropolymer segments is reported. The synthetic method is based on chain transfer emulsion polymerization of fluoromonomers and their subsequent employment as macroinitiators in atom transfer radical polymerization (ATRP) of non-fluorinated vinyl monomers. Trichloromethyl-terminated copolymers of vinylidene difluoride (VDF) and hexafluoropropylene (HFP), possessing molecular weights up to 25 000 g/mol, were obtained by emulsion polymerization in the presence of chloroform and used to initiate the ATRP of styrene (St) and methyl methacrylate (MMA) to form a series of P(VDF-*co*-HFP)-*b*-PS and P(VDF-*co*-HFP)-*b*-PMMA block copolymers. NMR, GPC, DSC, and TEM analysis confirmed the compositions of the block copolymers. The polymers exhibited a phase-separated morphology in the solid state and possessed distinct glass transition temperatures associated with fluoropolymer, PS, and PMMA domains.

Introduction

Block copolymers are of great scientific and technological importance. They have attracted considerable attention as thermoplastic elastomers, compatibilizers, surfactants, dispersants, emulsifiers, and foam stabilizers.[1] Block copolymers containing fluoropolymer segments would be particularly interesting, and potentially useful, because the incorporation of fluoropolymer would raise the chemical resistance and thermal stability of the polymer and lower the surface energy. Such block copolymers would also aid miscibility of polymer blends based on fluoropolymers and non-fluoropolymers by modifying the interface between the two dissimilar polymers: Only a few reports of successful blending of fluoropolymers with non-fluorinated polymers exist.[2]

Fluorine-containing block copolymers are also of interest as surfactants for polymerizations performed in supercritical carbon dioxide (scCO_2).[3] For example, poly(fluoroalkyl methacrylate)-*b*-PMMA block copolymers stabilize dispersion polymerization mixtures of MMA in scCO_2, leading to higher yields and higher molecular weight products.[3] A conclusion of this work is that the synthesis of fluorine-containing block copolymer surfactants possessing higher molecular weight and higher fluorine content may lead to even better surfactants.

Despite decades of research, there are few examples of block copolymers containing fluoropolymer and non-fluoropolymer sequences. For ease of discussion, fluorine-containing block copolymers can be considered to fall into one of two classes:[4] side chain fluorinated block copolymers, in which fluorinated chains are grafted onto the main chain of a non-fluorinated polymer, and main chain fluorinated block copolymers. Examples of the former are fluorinated (meth)acrylate block copolymers.[5] Main chain fluorinated block copolymers are much more difficult to synthesize because fluoromonomers cannot readily be synthesized by living ionic polymerization[6] or pseudo-living radical polymerization.[7−9]

Halogenated alkanes, such as $CHCl_3$, CCl_4, and $R-CCl_3$ derivatives, have been employed as initiating species in the ATRP of styrene and (meth)acrylates.[10] One approach to prepare fluorinated main chain block copolymers is to synthesize halogen-terminated fluoropolymers by means of telomerization and use them to initiate ATRP of a non-fluorinated monomer: Telomerization of vinylidene difluoride in the presence of $BrCF_2CF_2Br$ provided α,ω-dibrominated PVDF, which was subsequently used to initiate the ATRP of styrene to form PS-*b*-PVDF-*b*-PS triblock copolymers.[11] Furthermore, PVDF, terminated with trichloromethyl groups, prepared by telomerization of vinylidene difluoride in the presence of chloroform, initiates the ATRP of styrene, methyl methacrylate, methyl acrylate, and butyl acrylate to yield various diblock copolymers.[12] The recognized drawback of the telomerization approach is the low molecular weight of the fluoropolymer segments produced: the reported M_n of the PVDF segment was <2500 g/mol—too small for the block copolymers to adopt true fluoropolymer characteristics. It is desirable to devise synthetic methodology for the preparation of halogen-terminated fluoropolymers that possess higher molecular weights than currently available.

In this paper, we build upon previous successes described above and demonstrate a modified strategy, based on chain transfer polymerization, to obtain higher molecular weight, halogen-terminated fluoropolymers. Specifically, vinylidene difluoride (VDF) and hexafluoropropylene (HFP) are copolymerized by emulsion copolymerization in the presence of a halogenated chain transfer agent, chloroform, to prepare poly(VDF-*co*-HFP) possessing halogenated termini (Scheme 1).[10c,13] Fluoropolymer macroinitiators prepared this way were used to initiate the ATRP of styrene or MMA to form block copolymers P(VDF-*co*-HFP)-*b*-PS and P(VDF-*co*-HFP)-*b*-PMMA, respectively, according to Scheme 2.

Experimental Section

Materials. Vinylidene difluoride (VDF, Lancaster Synthesis, 99+%), hexafluoropropylene (HFP, Aldrich, 99+%), potas-

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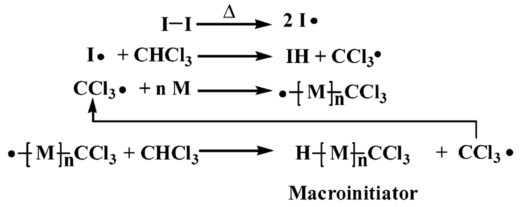
Scheme 1. Mechanism for Chain Transfer Polymerization



sium persulfate (KPS, Allied Chemical, reagent grade), sodium metabisulfite (Anachemia, anhydrous, reagent grade), pentadecafluorooctanoic acid (Aldrich, 96%), chloroform (Caledon, spectrograde), 2,2′-dipyridyl (bpy, Aldrich, 99+%), and copper(I) chloride (CuCl, Aldrich, 99.995+%) were used as received. Styrene (St, Aldrich, 99+%) and methyl methacrylate (MMA, BDH, reagent grade) were washed twice with aqueous 5% NaOH and twice with water, dried overnight with $MgSO_4$, distilled in the presence of CaH_2 at 40 °C under reduced pressure, and stored under N_2 at −20 °C. *n*-Butyl acetate (Caledon, reagent grade) was refluxed with small portions of $KMnO_4$, distilled in the presence of CaH_2 under reduced pressure, and stored under N_2 at −20 °C.

Emulsion Polymerization. A procedure for polymerization is as follows. To a 160 mL pressure vessel (Parr Instruments) equipped with a 600 psi pressure relief valve and a magnetic stir bar, a mixture of 100 mL of water, 0.80 g of KPS, 0.58 g of $Na_2S_2O_5$, 0.04 g of pentadecafluorooctanoic acid, and the required amount of chloroform was added. An initial monomer mixture comprising of 45 mol % HFP and 55 mol % VDF was introduced into the reactor. The temperature was maintained at 55 °C and its pressure at 300 psi by supplying to the vessel a supplemental monomer mixture of 20 mol % HFP and 80 mol % VDF.[14] Reaction times were varied from 4 to 10 h depending on the concentration of chain transfer agent. The resulting polymer latex was coagulated by freezing, and the fluoropolymer was washed with water and ethanol. The crude polymer was purified by repeated dissolution in acetone and reprecipitation in ethanol. Samples were dried at 50−60 °C under vacuum to yield white polymers. ^{19}F NMR (d_6-acetone) δ (ppm): −74.7, $-CF_2-CF(CF_3{}^*)-CH_2-CF_2-$; −90.9, $-CH_2-CF_2{}^*-CH_2-CF_2-$; −109.9 $-CH_2-CF_2{}^*-CF_2-CF(CF_3)-$; −117.9, $-CH_2-CF_2-CF_2{}^*-CF(CF_3)-$; −183.5, $-CF_2-CF^*(CF_3)-CH_2-CF_2-$. The compositions of the P(VDF-*co*-HFP) copolymers was calculated by NMR according to published methods[15] and found to be 16 ± 2% mol % HFP and 84 ± 2% mol % VDF.

ATRP. The trichloromethyl-terminated fluoropolymer (macroinitiator), solvent, catalyst, and monomer were introduced into a 25 mL flask equipped with a stopcock and a magnetic stir bar. Reactant quantities and specific reaction conditions are provided in the Results section. Following three freeze−pump−thaw cycles, the reaction mixture was heated under a nitrogen blanket to 110 °C. The polymerization was terminated by dissolving the mixture in THF, followed by precipitation in ethanol. The polymer was soluble in THF and further purified through a silica gel 60 (EM Science) column. Individual reaction conditions and yields are presented in later sections of this report. P(VDF-*co*-HFP) copolymers were insoluble in chloroform; the corresponding block copolymers for which the polystyrene segment length was comparable to or greater than that of the fluoropolymer were soluble. Because of this difference in solubility, unreacted macroinitiator was readily separated and quantified: >98% of the macroinitiator was found incorporated into block copolymers.

Measurements. Gel permeation chromatography (GPC) was performed using three μ-Styragel columns, a Waters 510 HPLC, polystyrene standards, THF eluant, and a Waters 410 differential refractometer. ^{1}H NMR spectra were recorded on a 400 MHz Bruker AMX400 spectrometer in d_6-acetone; ^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer, and chemical shifts were measured with respect to trichlorofluoromethane ($CFCl_3$). DSC measurements were carried out using a heating rate of 10 °C/min from −100 to 200 °C on ~12 mg samples, on a SII, EXSTAR 6000-DSC 6200 (Seiko Instruments Inc.). Elemental analysis was performed by Canadian Microanalytic Services Ltd., Vancouver.

Samples for transmission electron microscopy (TEM) were prepared as follows: Polymer films, ~0.1 mm thick, were cast from THF solution and stained with ruthenium tetroxide (RuO_4) vapor for 4 h. The RuO_4 staining solution was prepared in situ by dissolving 0.04 g of $RuCl_3{\cdot}3H_2O$ (Aldrich) in 2 mL of sodium hypochlorite solution (Aldrich).[16] Samples were embedded in Spurr epoxy resin, sectioned to yield slices ~100 nm thick, using a Reichert OM3 microtome, and picked up on copper grids. Electron micrographs were taken with a Hitachi H7600 transmission electron microscope using an accelerating voltage of 80 kV.

Results and Discussion

Synthesis of Fluoropolymer Macroinitiators. Emulsion copolymerization of VDF and HFP using $CHCl_3$ as the chain transfer agent was carried out as described above. An important consideration in this work is the necessity of synthesizing trichloromethyl-terminated fluoropolymers that are soluble in solvents compatible with ATRP. Unfortunately, many fluoropolymers are poorly soluble in common solvents. Poly(tetrafluoroethylene) (PTFE), a highly crystalline polymer, is insoluble in all solvents. Poly(vinylidene difluoride) (PVDF), a partially crystalline polymer, is soluble in dipolar aprotic solvents such as DMA, DMF, DMSO, and NMP.[17] The solubility of PVDF in common solvents is known to be improved by incorporating small amounts of hexafluoropropylene (HFP), which disrupts crystallinity. VDF was therefore copolymerized with HFP via chain transfer emulsion polymerization, in the presence of chloroform, to form readily soluble, fluorine-containing macroinitiators. It was found that 16 mol % HFP was sufficient to render the copolymers soluble in

Scheme 2. Preparation of Fluorine-Containing Block Copolymers by Chain Transfer Emulsion Polymerization and ATRP

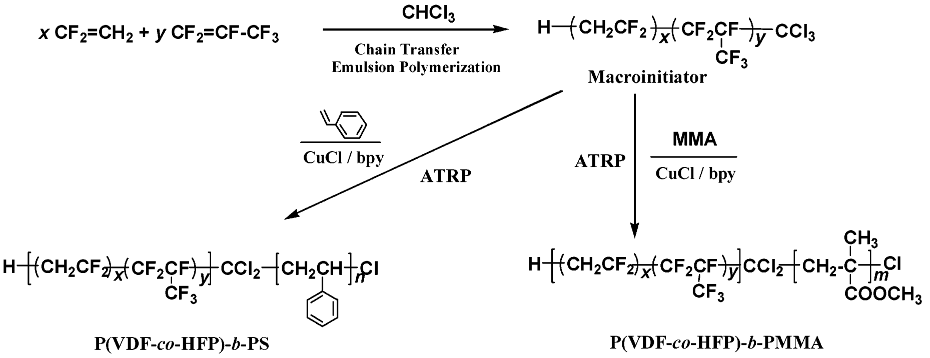


Table 1. Selected Properties of Poly(VDF-*co*-HFP) Prepared by Emulsion Polymerization of VDF and HFP in the Presence of Chloroform

P(VDF-*co*-HFP)	[$CHCl_3$] (M)	M_n (g/mol)[a]	PDI[b]	Cl (wt %)[c]	M_n (g/mol)[d]
1	0.625	1900	1.2	4.58	2300
2	0.187	3900	1.3	1.92	5500
3	0.125	6500	1.3	1.22	8700
4	0.062	8100	1.5	0.93	11400
5	0.037	14000	1.4	0.62	17200
6	0.031	16700	1.5	0.50	21300
7	0.012	24400	1.8	0.31	34300
8	0.000	N/A[e]			

[a] Determined by GPC using polystyrene standards. [b] Polydispersity index (M_w/M_n). [c] Determined by elemental analysis. [d] Calculated from the chlorine content, assuming each polymer chain possesses one CCl_3 terminal group, $M_n = [(\text{Cl wt fraction})^{-1} \times 35.45\ \text{g/mol} \times 3]$. [e] Gelatinous and insoluble in THF.

solvents such as acetone, THF, and ethyl acetate. Table 1 lists molecular weight and polydispersity indices, as estimated by GPC, of fluoropolymer macroinitiators as a function of concentration of chain transfer agent. Consistent with the theory of chain transfer polymerization is the observation that molecular weight increases as [$CHCl_3$] decreases. The polydispersity index increases with decreasing [$CHCl_3$] but nevertheless remains <1.5 except for the highest molecular weight polymers obtained. The molecular weight of macroinitiators produced varied from 2000 to 25 000 g/mol depending on the concentration of chloroform. When no chloroform was included in the polymerization (polymer 8, Table 1), the resulting copolymer was not completely soluble in THF, presumably due to cross-linking, and formed a gel.

It was intended to synthesize fluoropolymers possessing both H- and CCl_3-termini. First, the composition of initiator and chain transfer agent were chosen so that monomer polymerization was initiated by $^{\bullet}CCl_3$ radicals rather than persulfate radicals. This was achieved by having the concentration of $CHCl_3$ much higher than dissolved monomer so that persulfate radicals, produced by thermolysis, preferentially abstract H atoms from $CHCl_3$, forming $^{\bullet}CCl_3$. Second, because of the very low concentration of radicals in radical polymerization, the concentration of $CHCl_3$ was intended to be very much larger than either $^{\bullet}CCl_3$ or polymer radicals so that propagating polymer radicals are terminated by chain transfer from $CHCl_3$ rather than radical−radical coupling.

The chlorine content of each polymer was determined by elemental analysis. With the assumption that each fluoropolymer is terminated by a trichloromethyl group, the number-average molecular weight was calculated using $M_n = (1/\text{Cl wt fraction}) \times 35.45\ \text{g/mol} \times 3$. The molecular weights determined by GPC are observed to be 20−30% lower than that calculated based on chlorine content. The discrepancy most likely results from the use of polystyrene standards in the GPC analysis and the absence of reliable K and α values for P(VDF-*co*-HFP) copolymers.

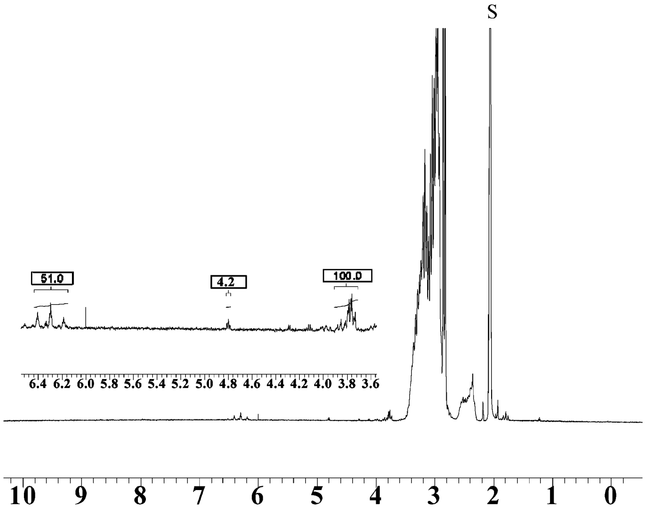


Figure 1. ^1H NMR spectrum of P(VDF-*co*-HFP) macroinitiator (polymer 5, Table 1, M_n = 14 000 g/mol).

The presence of the trichloromethyl terminal group was confirmed by ^1H NMR of fluoropolymer 5 (Figure 1). Peaks at 2.8−3.5 ppm are due to head-to-tail structures of VDF sequences, while peaks observed between 2.3 and 2.6 ppm are due to head-to-head or tail-to-tail structures of VDF sequences.[18] The small peaks between 3.7 and 3.8 ppm (see inset) are due to trichloromethyl structures of $-CF_2-CH_2^*-CF_2-CCl_3$ or $-CF_2-CH_2^*-CCl_3$. Small peaks between 6.2 and 6.4 ppm are also observed which are associated with H-terminated chain ends ($-CF_2-CH_2-CF_2H^*$ or $-CH_2-CH_2-CF_2H^*$).[18] In principle, the ratio of integrated signals between 3.7 and 3.8 ppm and between 6.2 and 6.4 ppm should provide an estimation of the ratio of CCl_3- to H-terminated fluoropolymer chains. In practice, the low signal-to-noise ratio diminished the method's accuracy. This ratio was calculated to be 1.6 ± 0.5, which is interpreted as providing reasonable evidence that one terminal group is not in large excess of the other. Small peaks due to $KO-SO_2-O-CH_2^*-CF_2-$ terminal groups were observed at 4.7−4.8 ppm. The ratio of integrals indicates the ratio of CCl_3-termini to persulfate-termini was 1:0.04; that is, at least 96% of fluoropolymer chains possess CCl_3-termini. This is consistent with the observation that >98% of the fluoropolymer initiates ATRP polymerization of vinyl monomers, as indicated in the Experimental Section.

Block Copolymerization of P(VDF-*co*-HFP) with Styrene and MMA via ATRP. CCl_3-terminated P(VDF-*co*-HFP) copolymers (polymers 1−7, Table 1) initiated the ATRP of styrene according to Scheme 2. Table 2 lists monomer feed ratios, reactant concentrations, and reaction conditions employed. One of the features of ATRP is that molecular weights can be predetermined by the ratio of monomer to initiator concentration. For reasons not discussed here, our interest was to prepare block copolymers with relatively short polystyrene block lengths. Hence, some polymerizations were terminated prior to high conversion. The estimated molecular weight of block copolymers was calculated using eq 1

$$M_n = M_{n(\text{macro})} + ([\text{St}]_0/[\text{Macro}]_0)M_{(\text{St})}C\ (\%) \qquad (1)$$

where M_n and $M_{n(\text{macro})}$ represent the theoretical and macroinitiator number-average molecular weight; $M_{(\text{St})}$ is the molecular weight of styrene; $[\text{St}]_0$ and $[\text{Macro}]_0$ represent the initial styrene and macroinitiator concentrations; and C represents percent conversion of styrene. As observed in Table 2, calculated values were in reasonable agreement compared to experimentally estimated values obtained by GPC.

Verification that polymerization proceeds by ATRP, according to Scheme 2, was provided by monitoring the

Table 2. ATRP of Styrene Initiated by the Poly(VDF-*co*-HFP) Macroinitiators (for Molecular Weight of Macroinitiators, See Table 1)

						P(VDF-*co*-HFP)-*b*-PS		
P(VDF-*co*-HFP)	$[St]_0$ (M)	[bpy] (M)	[Macro] (M)	time (h)	conv[a] (%)	M_n (g/mol)[b]	M_w/M_n[b]	M_n (g/mol)[c]
polymer 1	4.1	0.37	0.051	24	96.7	10 600	1.3	9 900
polymer 2	3.3	0.42	0.080	33	78.5	7 500	1.2	7 300
polymer 3	4.8	0.32	0.029	19	62.2	17 000	1.3	17 200
polymer 4	2.1	0.35	0.033	24	64.4	11 900	1.4	12 300
polymer 5	4.6	0.18	0.007	24	24.3	23 100	1.4	30 600
polymer 6	1.8	0.18	0.015	7	18.6	18 000	1.5	19 000
polymer 7	3.1	0.33	0.007	39	21.6	28 300	1.5	34 800

[a] Conversions were calculated gravimetrically. [b] Determined by GPC using polystyrene standards. [c] Theoretical molecular weight, calculated using eq 1.

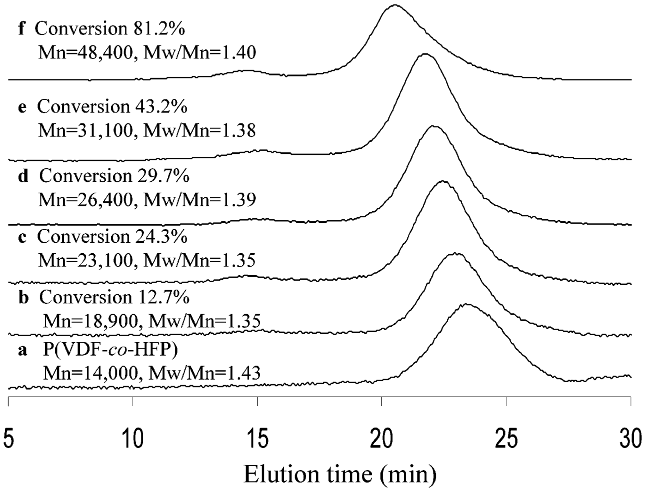


Figure 2. Evolution of GPC traces for the ATRP of styrene as a function of monomer conversion using P(VDF-*co*-HFP) macroinitiator (polymer 5, Table 1, M_n = 14 000 g/mol). $[\text{Macroinitiator}]_0 = 7.0 \times 10^{-3}$ M, [bpy] = 3[CuCl] = 0.18 M, $[St]_0$ = 4.6 M. Solvent: butyl acetate, T = 110 °C.

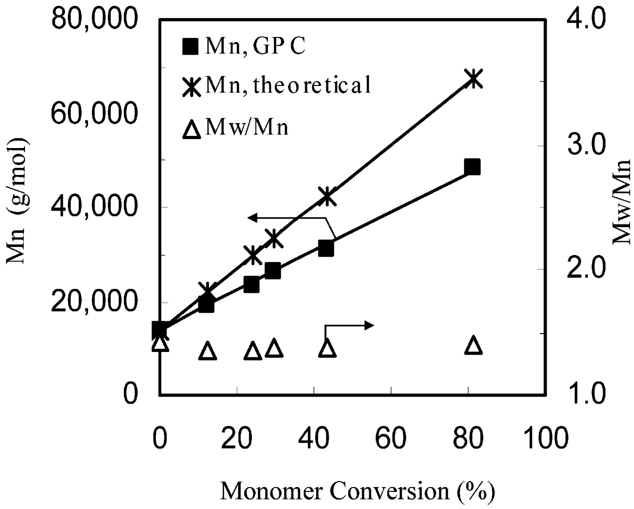


Figure 3. Dependence of M_n and polydispersity index on monomer conversion for the ATRP of styrene using P(VDF-*co*-HFP) macroinitiator (polymer 5, Table 1, M_n = 14 000 g/mol). $[\text{Macroinitiator}]_0 = 7.0 \times 10^{-3}$ M, [bpy] = 3[CuCl] = 0.18 M, $[St]_0$ = 4.6 M. Solvent: butyl acetate, T = 110 °C. The theoretical values, M_n, were calculated using eq 1.

evolution of GPC curves. This is demonstrated in Figure 2 for block copolymers prepared from polymer 5, Table 1, which possessed a M_n of 14 000 g/mol and PDI of 1.43. Curves a–f show the evolution of the GPC curves upon initiation and propagation of styrene. The curves shift left with monomer conversion, indicating a gradual increase in molecular weight. At high monomer conversion a minor peak was observed at an elution time of 14 min, representing a much larger molecular weight polymer (M_n = 850 000 g/mol). The mass fraction of this higher molecular weight polymer was calculated to be only 2.5 wt % of the total polymer obtained and its mole fraction, therefore, significantly less.

No evidence, such as multimodal GPC peaks, suggesting double or triple initiation at the CCl_3 terminus was observed either for the polymers reported or for numerous other polymers prepared (but not reported) related to this study. Neither has such evidence been observed in other studies of $-CCl_3$ macroinitiators[12,19,20]—it is implicitly accepted that the terminal groups are single initiator units.

Figure 3 shows a plot of GPC-determined molecular weight and polydispersity index as a function of monomer conversion for block copolymers prepared from polymer 5 (Table 1). M_n increases linearly with conversion while the polydispersity index remains low. Figure 3 also plots the theoretical evolution of M_n. These values are higher than the experimental, again due to the GPC technique underestimating M_n because the fluoropolymer segment decreases hydrodynamic volumes compared to polystyrene homopolymer. The linear relationship implies that the trichloromethyl-terminated fluoropolymer does indeed initiate the controlled radical polymerization of styrene. Figure 4 plots the time dependence of $\ln([M_0]/[M])$. The linear relationship indicates that the polymerization is first-order with respect to monomer and that the concentration of active species is constant throughout the reaction.

In a manner similar to the preparation of fluoropolymer–polystyrene block copolymers, P(VDF-*co*-HFP) macroinitiators were found to initiate the ATRP of MMA. This is exemplified in Figure 5, which shows the molecular weight of the macroinitiator increasing following initiation and propagation of MMA. Because of the relative ease of activation of the dormant species,[9] ATRP of MMA was much faster compared to that of styrene. For example, it took only 2.3 h to reach >80% MMA conversion, whereas it took 104 h for styrene, under the same experimental conditions.

Characterization. Figure 6 shows typical ^{1}H NMR spectra of a P(VDF-*co*-HFP) macroinitiator (Figure 6a), a P(VDF-*co*-HFP)-*b*-PS block copolymer (Figure 6b), and a P(VDF-*co*-HFP)-*b*-PMMA block copolymer (Figure 6c). The groups of peaks at 3.5–2.3 ppm, in the spectrum corresponding to P(VDF-*co*-HFP) macroinitiator, are attributed to head–tail, head–head, and tail–tail structures of VDF sequences and to protons associated with HFP. The same signature peaks are present in the block copolymers (Figure 6b,c). P(VDF-*co*-HFP)-*b*-PS possesses additional peaks at 7.4–6.5 ppm (aryl, 5H), 1.3–

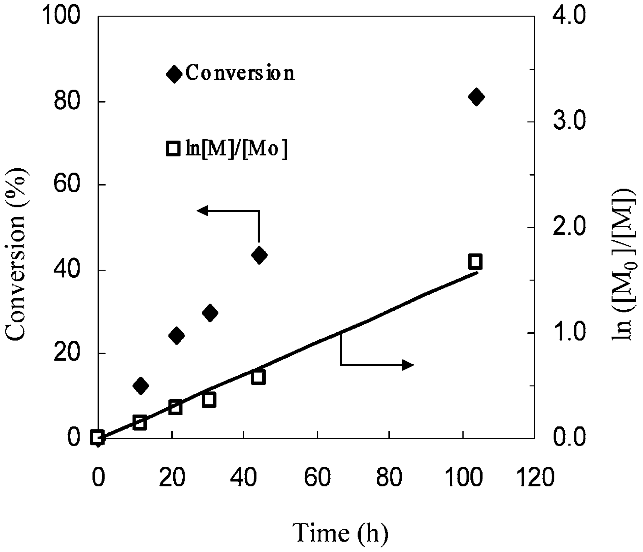


Figure 4. Dependence of monomer conversion on reaction time and first-order plots for the ATRP of styrene using P(VDF-*co*-HFP) macroinitiator (polymer 5, Table 1, $M_n = 14\,000$ g/mol). $[\text{Macroinitiator}]_0 = 7.0 \times 10^{-3}$ M, [bpy] = 3[CuCl] = 0.18 M, $[\text{St}]_0 = 4.6$ M. Solvent: butyl acetate, $T = 110$ °C.

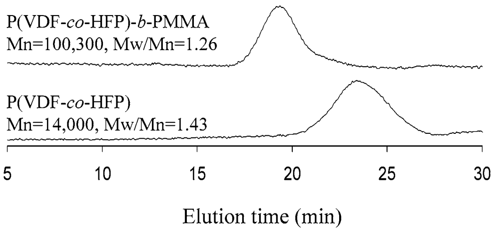


Figure 5. GPC traces of P(VDF-*co*-HFP)-*b*-PMMA block copolymer and P(VDF-*co*-HFP) macroinitiator (polymer 5, Table 1, $M_n = 14\,000$ g/mol). Reaction conditions: $[\text{Macroinitiator}]_0 = 7.0 \times 10^{-3}$ M, [bpy] = 3[CuCl] = 0.18 M, $[\text{MMA}]_0 = 4.6$ M. Solvent: butyl acetate, $T = 110$ °C; time: 2.3 h; MMA conversion: 82.3%.

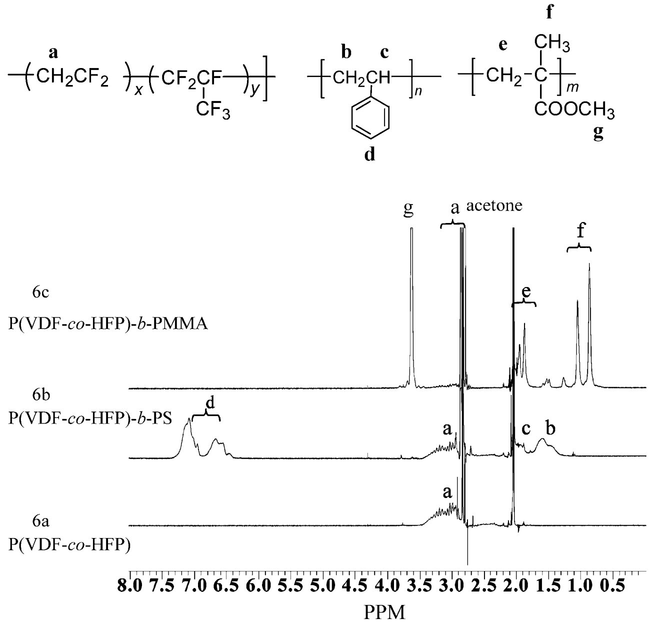


Figure 6. 400 MHz ^{1}H NMR spectra of fluorine-containing block copolymers. Solvent: d_6-acetone.

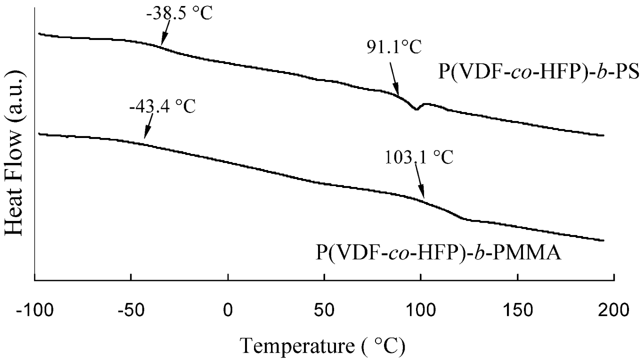


Figure 7. DSC analysis of the fluorine-containing block copolymers possessing polystyrene ($M_n = 26\,400$ g/mol, see Figure 1d) and PMMA ($M_n = 100\,300$ g/mol, see Figure 5).

1.7 ppm (methylene, 2H), and 1.8−2.0 ppm (benzylic, 1H). Similarly, in Figure 6c, additional peaks assigned to PMMA at 3.6 ppm (ester methyl, 3H), 0.8−1.3 ppm (methyl, 3H), and 1.8−2.1 ppm (methylene, 2H) are observed in P(VDF-*co*-HFP)-*b*-PMMA. The peaks for the PMMA sequence agrees with those provided in the literature.[21]

The T_g of P(VDF-*co*-HFP)-*b*-PS and P(VDF-*co*-HFP)-*b*-PMMA initiated by the same fluorine-containing macroinitiator ($M_n = 14\,000$) were determined by DSC. Figure 7 shows DSC curves of P(VDF-*co*-HFP)-*b*-PS ($M_n = 26\,400$ g/mol) and P(VDF-*co*-HFP)-*b*-PMMA ($M_n = 100\,300$ g/mol). Both exhibit two glass transition temperatures. Previous studies by Bonardelli et al.[22] indicate that the T_g of P(VDF-*co*-HFP) copolymers possessing HFP contents 11 and 16.3 mol % were −33 and −29 °C, respectively. In the present work, the T_g of the P(VDF-*co*-HFP) segment is −40 ± 3 °C. The origin of this difference is either the presence of the nonfluorinated block or differences in the statistical distribution of HFP along the fluoropolymer segment. The T_g of the polystyrene and PMMA segments are 91 and 103 °C, respectively. T_g can be molecular weight dependent: PS exhibits a T_g of up to 110 °C for molecular weights >10 000 g/mol but much lower for molecular weights less than this. The molecular weight of the polystyrene segments in the block copolymer analyzed by DSC was estimated to be ~12 000 g/mol, yet the measured T_g for this segment was still quite low (91 °C). Moreover, the measured T_g of the PMMA segment in P(VDF-*co*-HFP)-*b*-PMMA block copolymer was 103 °C (which is also lower than that of the MMA homopolymer, 105−111 °C)[17] even though its molecular weight was >80 000 g/mol. A logical explanation is that PS domains in the films are too small to fully adopt the properties of PS homopolymer, and because the surrounding fluoropolymer possesses a much lower T_g, the T_g of the PS domains is lower than that of the corresponding homopolymer.

The morphology of films of P(VDF-*co*-HFP)-*b*-PS was examined by TEM (Figure 8). Ruthenium tetroxide (RuO_4) was used to stain polystyrene segments. The lighter regions therefore represent P(VDF-*co*-HFP). A “sea−island” morphology was observed for all TEM images. The size of the polystyrene domains for the block copolymers shown in Figure 8a,b varies between 10 and 30 nm. The density of polystyrene domains increases with increasing polystyrene content as indicated in the comparison of parts a−c of Figure 8. As the PS content is increased to >50 wt %, the polystyrene domains coalesce to form a continuous phase. Typical lamellae or cylindrical morphologies were not observed in these copolymer films. However, when the polystyrene segments of the copolymer are sulfonated by

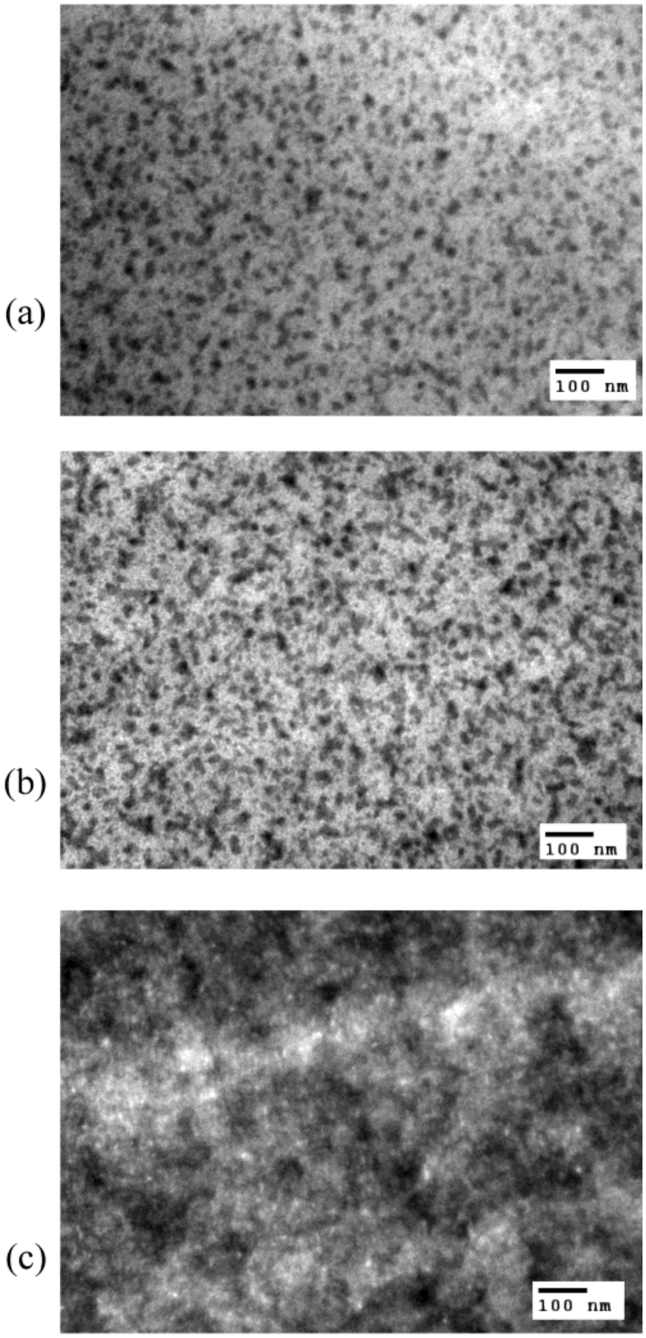


Figure 8. TEM images of P(VDF-*co*-HFP)-*b*-PS: (a) M_n = 18 900 g/mol, St % = 35 wt % (see Figure 1b); (b) M_n = 23 100 g/mol, St % = 40 wt % (see Figure 1c); (c) M_n = 31 100 g/mol, St % = 55 wt % (see Figure 1e).

postsulfonation, and cast to form films, typical block copolymer morphologies are indeed observed.[23] This leads to the conclusion that the TEMs represent non-equilibrium morphologies. Meaningful TEM images of P(VDF-*co*-HFP)-*b*-PMMA samples were not obtainable as neither PMMA nor P(VDF-*co*-HFP) segments are stained by RuO_4.[24]

Conclusions

Macroinitiators comprising of poly(vinylidene difluoride-*co*-hexafluoropropylene) were prepared by chain transfer emulsion polymerization. The molecular weights of fluoropolymer macroinitiators were varied from 2000 to 25 000 g/mol by controlling the concentration of chain transfer agent. These polymers initiated the ATRP of styrene and methyl methacrylate. A series of fluorine containing block copolymers were successfully synthesized. The methodology of producing trichloromethyl-terminated vinylic polymers by chain transfer polymerization may prove a useful strategy for the general synthesis of macroinitiators for subsequent preparation of novel block copolymers. Applied to fluorinated monomers, this technique provides access to novel polymers that may find potential applications as compatiblizers, surfactants for supercritical CO_2 polymerization, and novel materials and thin films.

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