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Graft Copolymers from Poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) via Atom Transfer Radical Polymerization

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ABSTRACT: We report the grafting of polystyrene (PS) and poly(*tert*-butyl acrylate) (P*t*BA) from poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (P(VDF-*co*-CTFE)) via atom transfer radical polymerization (ATRP). The initiating sites on P(VDF-*co*-CTFE) for the graft copolymerization are the secondary chlorines, indicated by the model reactions using poly(chlorotrifluoroethylene) (PCTFE) oligomer and the control experiment using poly(vinylidene fluoride) (PVDF). The formation of graft copolymers, P(VDF-*co*-CTFE)-*g*-PS and P(VDF-*co*-CTFE)-*g*-P*t*BA, was confirmed by ^{1}H NMR, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), and atomic force microscopy (AFM) measurements. The hydrolysis of P*t*BA grafts in P(VDF-*co*-CTFE)-*g*-P*t*BA resulted in amphiphilic graft copolymers with hydrophilic poly(acrylic acid) (PAA) side chains. The synthetic approach reported here offers a convenient way to modify commercial fluoropolymers containing CTFE units. The resultant graft copolymers may find potential applications such as materials for filtration membranes.

Introduction

Fluoropolymers are known to possess unique properties such as low surface energy, high chemical and thermal stability, and good mechanical properties. They have been widely used for various industrial applications including thermal insulators, chemically resistant materials, lubricants, filter membranes, and electrical insulators. Fluoropolymers, however, are normally highly hydrophobic and solvophobic. So they have certain disadvantages, such as poor solubility, wettability, and miscibility. They are also susceptible to fouling because of the adsorption of proteins and oils.[1−3] These problems limit their applications in certain fields such as filtration membranes and medical devices. Modification of commercial fluoropolymers has attracted particular interest due to the desired properties of the modified polymers. Indeed, properties such as wettability, amphiphilicity, biocompatibility, solubility, compatibility with other polymers, and adhesion to surfaces can be greatly improved by graft copolymerization of comonomers from the backbone of fluoropolymers. For example, amphiphilic graft copolymers based on fluoropolymers show enhanced surface properties, such as biocompatibility, antifouling, and reduced static charge buildup.[4] Depending on the nature of the comonomer, graft copolymers may possess specific properties while retaining the desirable properties of the parent fluoropolymers.

So far, graft copolymerization of comonomers from commercial polymers is mainly accomplished by free radical routes. Radicals on the parent polymer chains, that serve as initiating sites for graft copolymerization, are produced by exposure to ionizing radiation,[5,6] using a free-radical initiator,[7] or by thermal decomposition of peroxide groups obtained by ozonolysis.[8,9] However, these grafting techniques offer little or no control over the structure of the resultant graft copolymers. In addition, in these free-radical routes nonpolymeric radicals are also produced that can initiate the homopolymerization of comonomer. Thus, mixtures of graft copolymers and homopolymers are obtained. Furthermore, backbone degradation and gelation can also occur as a result of uncontrolled free radical production, resulting in limited grafting density.

Recently, atom transfer radical polymerization (ATRP) has been successfully used to prepare well-defined graft copolymers based on the "grafting from" method, i.e., side chains are grafted from the backbone via ATRP initiated by the pendant initiating groups on the backbone polymers.[10−13] In ATRP, alkyl halides with radical stabilizing substituents (such as aryl, carbonyl, and allyl groups) on the α-carbon have been widely used as initiators. So far, alkyl bromides and alkyl chlorides offer the best molecular weight control. Commercial halogenated polyolefins, such as poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), poly(chlorotrifluoroethylene) (PCTFE), and their copolymers, comprise monomer units with pendant secondary halogen atoms, which are potential ATRP initiators. In principle, graft copolymerization from these polymers should be possible to prepare functional graft copolymers. However, it is generally believed that the secondary chlorines and fluorines in these halogenated polyolefins are too strongly bonded to serve as ATRP initiating sites. It has been reported that the PVC backbone remained intact during the graft copolymerization from a PVC possessing 1% of vinyl chloroacetate segments, which were utilized as the ATRP initiating sites.[14]

However, recently Mayes et al. succeeded in the direct graft copolymerization of methacrylates from PVDF via ATRP using secondary fluorine as the initiator.[4,15] Because of the expected low reactivity of secondary fluorine atoms, the initiating efficiency was often very low, which resulted in low grafting density. For example, only about 0.1% of the secondary fluorines in PVDF were able to initiate the graft copolymerization of *tert*-butyl methacrylate.[4] Furthermore, the strong C−F bond led to slow initiation compared to the rate of propagation, limiting the "living" nature of the polymerization. The low reactivity of the secondary fluorines also limits the choices of comonomers. Despite these disadvantages, the technique developed by Mayes et al. offers a simple way to produce functionalized derivatives

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Table 1. Characterization Results of the PCTFE Oligomer and P(VDF-*co*-CTFE)s

code	M_n (g/mol)[a]	PDI [a]	elemental analysis (wt %)				content of CTFE (wt %)[b]
			C	H	F	Cl	
PCTFE oligomer			18.02		41.8	38.8	
P(VDF-*co*-CTFE)-31008	1.77×10^5	1.52	35.93	2.82	59.0	3.65	11.99
P(VDF-*co*-CTFE)-31508	1.80×10^5	1.47	35.21	2.77	56.7	5.68	18.66

[a] Number-averaged molecular weight (M_n) and polydispersity index (PDI) from SEC measurements in DMF calibrated against polystyrene standards. [b] Calculated according to the content of chlorine from elemental analysis.

Table 2. Homopolymerization of Styrene (St) and Sequential Block Copolymerization of Styrene and *tert*-Butyl Acrylate (*t*BA) Initiated by PCTFE Oligomer

run no.	initiator/monomer	catalyst/ligand	[Cl]/[CuCl]/[Lig]/[M][a]	solvent (V_S/V_M)[b]	temp (°C)	time (h)	conv (%)	M_n ($\times 10^3$)[c]	PDI[c]
1	PCTFE/St	CuCl/PMDETA	1/0.8/0.8/80	NMP (1/11.5)	120	4	51.6	22.1	1.79
2	PCTFE/St	CuCl/PMDETA	1/0.8/0.8/80	NMP (1/1.15)	120	2.5	53.9	17.6	2.25[d]
3	PCTFE/St	CuCl/BPy	1/0.4/0.8/80	NMP (1/1.15)	120	10	36.7	8.56	1.60
4	polymer from run 3/*t*BA	CuCl/PMDETA	1[e]/0.8/0.8/160	NMP (1/1.15)	70	0.5	56.3	12.9	2.03

[a] [Cl]/[CuCl]/[Lig]/[M] is the initial molar ratio of chlorine, CuCl, ligand, and monomer. [b] V_S/V_M is the volume ratio between solvent and monomer. [c] Obtained from SEC in THF using polystyrenes as calibration standards. [d] Bimodal molecular weight distribution. [e] Calculated based on the monomer conversion in run 3.

of PVDF. The resultant graft copolymers have been found to be very useful as materials for functional filtration membranes.[16,17]

Here, we report the graft copolymerization of styrene and *tert*-butyl acrylate (*t*BA) from poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (P(VDF-*co*-CTFE)) via ATRP. Model reactions using poly(chlorotrifluoroethylene) (PCTFE) oligomer as ATRP initiator showed that the secondary chlorines in PCTFE were much more reactive than those in PVC with respective to radical generation under ATRP conditions, indicating the ability of fluorine atoms to activate the chlorines toward atom transfer.[18]

By hydrolyzing poly(*tert*-butyl acrylate) (P*t*BA) side chains of the graft copolymers, P(VDF-*co*-CTFE)-*g*-P*t*BA, amphiphilic graft copolymers with poly(acrylic acid) (PAA) side chains were prepared. These amphiphilic fluoropolymers have potential applications as in the preparation of filtration membranes with engineered surface properties.[19]

Experimental Section

Materials. PCTFE oligomer (liquid, molecular weight = 500−600 g/mol) was purchased from Polysciences Inc. and used without further purification. P(VDF-*co*-CTFE)-31008 and P(VDF-*co*-CTFE)-31508, which contain 3.65 and 5.68 wt % of chlorine, respectively, were provided by Solvay Solexis. These two copolymers have a pseudo-block structure with one VDF-rich block and one CTFE-rich block. The characterization results of the PCTFE oligomer and two P(VDF-*co*-CTFE)s are shown in Table 1.

Styrene (Aldrich, 99%) and *tert*-butyl acryale (Aldrich, 98%) were stirred over CaH_2 and vacuum-distilled before use. CuCl (Aldrich, 99.995+%), $CuCl_2$ (Aldrich, 99.999%), 2,2′-bipyridine (BPy, Acros, 99+%), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), *N*,*N*-dimethylformamide (DMF, Acros, HPLC grade), and *N*-methylpyrrolidinone (NMP, Acros, HPLC grade) were used as received without further purification.

Model Reactions. In the model reactions, poly(chlorotrifluoroethylene) (PCTFE) oligomer was used as ATRP initiator to polymerize styrene. In a typical experiment (run 3, Table 2), PCTFE oligomer (116 mg, containing 1.27 mmol of chlorine), BPy (156 mg, 1 mmol), styrene (10.422 g, 100 mmol), and NMP (10 mL) were added into a 100 mL Schlenk flask. The mixture was degassed via three cycles of freeze−pump−thaw, and the reaction flask was filled with N_2. Then, CuCl (50 mg, 0.5 mmol) was added, and the reaction mixture was degassed again followed by refilling the flask with N_2. The reaction mixture was stirred until a homogeneous solution was obtained. An initial sample was taken for the monomer conversion measurement. The polymerization was started by immersing the reaction flask in an oil bath at a temperature of 120 °C. During the polymerization, kinetics samples were taken from the reaction flask using N_2-purged syringes at desired time intervals. The samples were immediately diluted with deuterated chloroform ($CDCl_3$) followed by ^1H NMR measurements to determine the monomer conversion. After 10 h, the polymerization was stopped by cooling to room temperature and exposure to air. The reaction mixture was poured into 500 mL of methanol and the polymer precipitated. The resultant polymer was dried in a vacuum oven at 60 °C overnight.

The polystyrene synthesized in run 3 in Table 2 was further used as macroinitiator to polymerize *tert*-butyl acrylate (*t*BA) via ATRP. In a typical block copolymerization (run 4, Table 2), 1 g of polystyrene (containing 0.32 mmol of chlorine) was dissolved in 6.4 mL of NMP in the reaction flask, and then 4.55 g of *t*BA and 25.1 mg of CuCl (0.254 mmol) were added. After degassing, the reaction flask was filled with N_2. In a separate flask, 44.8 mg of PMDETA (0.259 mmol) was dissolved in 1.99 g of *t*BA. After degassing (and filling the flask with N_2), the PMDETA solution was transferred into the reaction flask using a N_2-purged syringe. An initial sample was taken for the monomer conversion measurement. The polymerization was started by immersing the reaction flask in an oil bath at a temperature of 70 °C. After half an hour, the polymerization was stopped by cooling to room temperature and exposure to air. Different from the polystyrene macroinitiator, the resultant copolymer did not precipitate in methanol. A turbid dispersion was obtained when the reaction mixture was poured into methanol. Addition of water (with the volume ratio between methanol and water of 4/1) facilitated the precipitation of the resultant polymer.

Graft Copolymerization of Styrene from P(VDF-*co*-CTFE). A typical graft copolymerization of styrene (run 2, Table 3) is described in the following. 1.0 g of P(VDF-*co*-CTFE)-31008 (containing 1.03 mmol of Cl) was dissolved in 15 mL of NMP in a 50 mL Schlenk flask, and then 4.61 g of styrene (44.33 mmol) was added into the P(VDF-*co*-CTFE) solution. After the addition of CuCl (86 mg, 0.87 mmol), the polymer solution was degassed through three cycles of freeze−pump−thaw, and then the flask was filled with N_2. Separately, 267 mg of 2,2′-bipyridine (BPy, 1.71 mmol) was dissolved in 5 mL of NMP in a 25 mL Schlenk flask, and the solution was degassed, followed by filling the flask with N_2. The bipyridine solution was then transferred into the reaction flask using a N_2-purged syringe. An initial sample was taken for the monomer conversion measurement. The reaction flask was then immersed in an oil bath at 120 °C. During the polymerization, kinetics samples were taken from the flask using N_2-purged syringes at desired time intervals. After 24 h, the polymerization was stopped by cooling to room temperature and exposure to air. The reaction mixture was diluted with acetone and then passed through a column filled with silica gel, followed by precipitation in methanol. The

Table 3. Graft Copolymerization of Styrene (St) from P(VDF-*co*-CTFE)s

run no.	initiator	catalyst/ligand	[Cl]/[CuCl]/[Lig]/[St][a]	solvent (V_S/V_M)[b]	temp (°C)	time (h)	conv (%)	M_n (× 10^5)[c]	PDI[c]	W_{PS} (%)[d]
1	31008	CuCl/PMDETA	1/0.9/0.8/42	DMF (3/1)	90		gel			
2	31008	CuCl/BPy	1/0.8/1.7/43	NMP (3.9/1)	120	24	33.7	2.94	1.75	57.0 (60.8)
3[e]	PVDF	CuCl/BPy	0/0.8/1.7/43	NMP (3.9/1)	120	24	34.7			
4	31508	CuCl/BPy	1/0.4/0.4/40	NMP (2/1)	120	12	25.0[f]	3.28	1.59	52.2 (62.6)

[a] [Cl]/[CuCl]/[Lig]/[St] is the initial molar ratio of chlorine, CuCl, ligand, and styrene. [b] V_S/V_M is the volume ratio between solvent and monomer (styrene). [c] Obtained from SEC in DMF using polystyrenes as calibration standards. [d] Weight percentage of polystyrene in the resultant graft copolymers determined by elemental analysis. (The data in the parentheses represent the calculated values based on the monomer conversion.) [e] Control experiment. [f] Estimated based on the first-order polymerization kinetics as shown in Figure 3a.

Table 4. Graft Copolymerization of *tert*-Butyl Acrylate (*t*BA) from P(VDF-*co*-CTFE)

run no.	initiator	catalyst/ deactivator/ligand	[Cl]/[CuCl]/ [$CuCl_2$]/[Lig]/ [*t*BA][a]	solvent (V_S/V_M)[b]	temp (°C)	time (h)	conv (%)	M_n (× 10^5)[c]	PDI[c]	W_{PtBA} (%)[d]
1	31508	CuCl/−/PMDETA	1/0.8/0/0.8/40	NMP (2.1/1)	100		gel			
2	31508	CuCl/$CuCl_2$/PMDETA	1/0.8/0.16/0.8/40	NMP (2.1/1)	90	0.75	31.6	5.73	1.52	70.9 (72.3)
3	31508	CuCl/$CuCl_2$/PMDETA	1/0.4/0.08/0.4/40	NMP (1.1/1)	70	20	20.6	2.75	1.73	52.6 (63.0)
4	31508	CuCl/−/PMDETA	1/0.8/0/0.8/41	NMP (1.1/1)	70	1	17.3	2.51	1.77	47.8 (59.3)
5	31508	CuCl/−/PMDETA	1/0.8/0/0.8/40	NMP (1.6/1)	60	3	25.7	2.64	2.45	59.8 (68.0)

[a] [Cl]/[CuCl]/[$CuCl_2$]/[Lig]/[*t*BA] is the initial molar ratio of chlorine, CuCl, $CuCl_2$, ligand, and *t*BA. [b] V_S/V_M is the volume ratio between solvent and monomer (*t*BA). [c] Obtained from SEC in DMF using polystyrenes as calibration standards. [d] Weight percentage of P*t*BA in the resultant graft copolymers determined by elemental analysis. (The data in the parentheses represent the calculated values based on the monomer conversion.)

resultant graft copolymer was dried in a vacuum oven at 60 °C overnight.

A control experiment (run 3, Table 3) using PVDF homopolymer (Polysciences Inc., molecular weight = 100 kg/mol) as macroinitiator was carried out in exactly the same manner as that described above (run 2, Table 3), except that 1.0 g of PVDF was used in the control experiment instead of P(VDF-*co*-CTFE)-31008.

Graft Copolymerization of *tert*-Butyl Acrylate from P(VDF-*co*-CTFE). A typical graft copolymerization of *tert*-butyl acrylate (*t*BA) (run 2, Table 4) is described in the following. 1.0 g of P(VDF-*co*-CTFE)-31508 (containing 1.6 mmol of Cl) was dissolved in 15 mL of NMP in a 50 mL Schlenk flask, and then 8.254 g of *t*BA (64.4 mmol) was added into the polymer solution. After the addition of CuCl (128 mg, 1.29 mmol) and $CuCl_2$ (35 mg, 0.26 mmol), the polymer solution was degassed through three cycles of freeze−pump−thaw, and then the flask was filled with N_2. Separately, 236 mg of PMDETA (1.36 mmol) was dissolved in 5 mL of NMP in a 25 mL Schlenk flask, and the solution was degassed, followed by filling the flask with N_2. The PMDETA solution was then transferred into the reaction flask using a N_2-purged syringe. An initial sample was taken for the monomer conversion measurement. The reaction flask was then immersed in an oil bath at 90 °C. During the polymerization, kinetics samples were taken from the flask using N_2-purged syringes at desired time intervals. After 45 min, the reaction mixture became very viscous. So the polymerization was stopped by cooling to room temperature and exposure to air. The reaction mixture was diluted with acetone and then passed through a column filled with silica gel, followed by precipitation in methanol. The resulted graft copolymer was dried in a vacuum oven at 60 °C overnight.

Hydrolysis of P(VDF-*co*-CTFE)-*g*-PtBA. 0.34 g of P(VDF-*co*-CTFE)-*g*-P*t*BA (run 2, Table 4) was dissolved in 25 mL of NMP, and then 1.6 mL of concentrated HCl solution (36.9%) was added. After stirring at 100 °C for 48 h, most solvent was removed via vacuum distillation. The residual solution was poured into a mixture of methanol and water (v/v = 2/1) to precipitate the resultant polymer. ^1H NMR measurements showed the complete hydrolysis of P*t*BA side chains.

Characterizations. Size exclusion chromatography (SEC) was used to determine the molecular weights and molecular weight distributions of the polymers. SEC measurements of the polymers synthesized from the model reactions were carried out in tetrahydrofuran (THF) at a flow rate of 1.0 mL/min, using three PLgel 5 μm Mixed-D columns, a Knauer K-501 HPLC pump, and a Knauer K-2301 RI detector. Linear polystyrenes were used as calibration standards. SEC measurements of P(VDF-*co*-CTFE)s and the graft copolymers were conducted in DMF containing 0.01 M lithium chloride at a flow rate of 1.0 mL/min at 50 °C, using PL-GPC 50 system with two PL ResiPore columns. Linear polystyrene standards were used to calibrate the column set.

^1H and ^{13}C NMR measurements were performed on a Bruker DPX 300 spectrometer. For the measurement of monomer conversion, kinetics sample (35−40 μL) was diluted with 0.6 mL of $CDCl_3$ and then was subjected to ^1H NMR measurement. The monomer conversion was calculated on the basis of the area ratio between the peak of the protons from the double bond of monomer and the peak of the methylene protons adjacent to the nitrogen atom in *N*-methylpyrrolidinone (solvent for polymerization).

C and H elemental analysis was performed on a 1−3 mg sample (precisely weighed to ±1 μg) through combustion at 1000 °C over a Pt combustion aide. The resultant CO_2 and H_2O were analyzed by selective thermal conductance detectors after calibration and blanking in a He stream. For the fluorine analysis, an Schoniger oxygen flask decomposition of a fluorine-containing sample was followed by a fluoride ion selective electrode determination of the captured gaseous products after adjusting the pH and ionic strength of the solution using standards and blanks. Chlorine was determined after an Schoniger flask decomposition of the compound. The chloride ion formed was determined using a chloridometer that titrates the chloride ion coulometrically with silver.

Differential scanning calorimetry (DSC) was performed using a Thermal Analysis Q1000 calorimeter. To avoid the influence of the thermal history, polymers were heated from 25 to 250 °C at 10 °C/min and then cooled to −90 °C at 10 °C/min. DSC thermograms were obtained during the second heating from −90 to 250 °C at 10 °C/min.

The morphology of P(VDF-*co*-CTFE) and P(VDF-*co*-CTFE)-*g*-PS was characterized using a Dimension IIIa atomic force microscope (AFM) from Digital Instruments/Veeco operated in tapping mode, using a silicon cantilever. As for the sample preparation, the polymers were dissolved in DMF with the concentration of 2 wt %, and the polymer solutions were spin-coated onto silicon wafer at 2000 rpm for 3 min under N_2. The samples were then annealed at 190 °C under vacuum for 20 h.

Results and Discussion

Model Reactions Using PCTFE Oligomer as ATRP Initiator. To determine the reactivity of secondary chlorines in poly(chlorotrifluoroethylene) (PCTFE) with respective of radical generation, copper-mediated atom transfer radical polymerizations (ATRP) of styrene were carried out using PCTFE

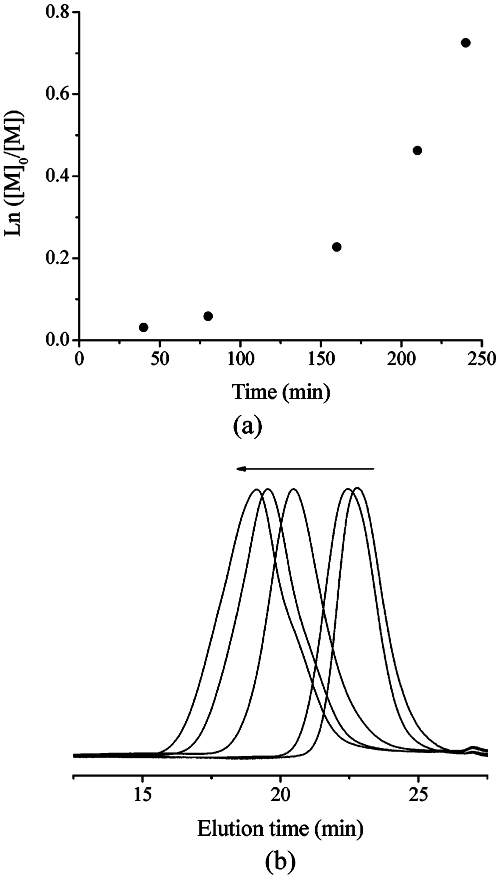
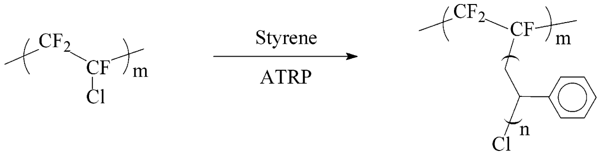


Figure 1. Heterogeneous ATRP of styrene initiated by PCTFE oligomer at 120 °C (run 1, Table 2); $0.8[\mathrm{Cl}]_0 = [\mathrm{CuCl}]_0 = [\mathrm{PMDETA}]_0 = 0.01[\mathrm{styrene}]_0 = 0.08$ M. (a) Semilogarithmic kinetics plot (where $[M]_0$ and $[M]$ represent the monomer concentration at the reaction time of 0 and t, respectively). (b) SEC traces of the resultant polymers at different polymerization times (from right to left: 40, 80, 160, 210, and 240 min).

Scheme 1. ATRP of Styrene Initiated by PCTFE Oligomer



oligomer as initiator (Scheme 1). High molecular weight PCTFE could not be used because it is insoluble in most of organic solvents. Commercially available ligands, such as 2,2′-bipyridine (BPy) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), were used in the model reactions.

Polymerization of styrene initiated by the PCTFE oligomer proceeded very rapidly when CuCl/PMDETA was used as the ATRP catalyst system with the molar ratio of Cl/CuCl/PMDTEA of 1/0.8/0.8 (runs 1 and 2, Table 2). Since the CuCl/PMDTEA (and also CuCl/BPy) complex is insoluble in styrene, polar solvents, like *N*-methylpyrrolidinone (NMP), were added in order to obtain a homogeneous polymerization system. When the amount of polar solvent was not enough, like in run 1 in Table 2, CuCl/PMDETA complex was not completely dissolved, and thus the reaction system was heterogeneous. Size exclusion chromatography (SEC) measurements showed that the molecular weight of polymer increased with increasing monomer conversion. However, the polymerization rate was not first-order with respect to the monomer concentration, as shown in Figure 1a. Obviously, the concentration of radicals increased with polymerization time. The acceleration of polymerization is most likely due to the slow initiation caused by the low solubility of CuCl/PMDETA complex in the reaction mixture. When more polar solvent (NMP) was added, such that the reaction mixture was homogeneous (run 2, Table 2), the polymerization exhibited perfect first-order kinetics with respect to the monomer concentration, which is characteristic for ATRP. However, the SEC traces of the resultant polymers show bimodal molecular weight distribution even at the initial stage of polymerization, indicating the occurrence of radical coupling, more than likely due to the high concentration of reactive radicals.

By using BPy as the ligand and decreasing the overall concentration of catalyst (run 3, Table 2), polymers with controlled molecular weights and relatively narrow molecular weight distribution were obtained. Although the polymerization was much slower in this case, first-order polymerization kinetics was observed, as shown in Figure 2a. The resultant polymer has a polydispersity index of 1.60, which is higher than that of linear polymers synthesized from typical ATRP. However, taking into account that the initiator we used is a mixture of multifunctional PCTFE chains with different degrees of polymerization, as indicated by the mass spectroscopy measurement (see the Supporting Information), the somehow broader molecular weight distribution of the resultant polymer is to be expected. The reason for the appearance of a faint shoulder at the low molecular weight side of the SEC traces shown in Figure 2b is unclear yet, but it may stem from the distribution of PCTFE oligomer and/or some possible side reactions (such as transfer reactions). The increase in molecular weight with monomer conversion (Figure 2c), in conjunction with the first-order polymerization kinetics, indicates that this polymerization process was living.

To further confirm that the polymerization discussed above was a living process, the resultant polystyrene was used as macroinitiator to polymerize *tert*-butyl acrylate (*t*BA). Indeed, the ATRP of *t*BA initiated by the polystyrene synthesized in run 3 in Table 2 proceeded very rapidly. The increase in the molecular weight (run 4, Table 2) indicates the successful block copolymerization, strongly supporting the living nature of ATRP initiated by PCTFE oligomer.

On the basis of the model reactions described above, it is clear that PCTFE oligomer was able to initiate homopolymerization of styrene and block copolymerization of styrene and *t*BA under ATRP conditions. Since PCTFE oligomer contains secondary chlorines and secondary fluorines, which both are potential ATRP initiators, it is necessary to distinguish whether the polymerizations were initiated by secondary chlorines exclusively or by both of them. Thus, the control experiment using poly(vinylidene fluoride) (PVDF) as the macroinitiator was carried out (which will be described in the next section), and the results showed that PVDF could not initiate ATRP of styrene under the polymerization conditions we used. Combining the results from both the model reactions and the control experiment, it is clear that the initiating site in PCTFE oligomer was the secondary chlorine. Compared with the secondary chlorines in poly(vinyl chloride) (PVC), which were found to be too strongly bonded to initiate ATRP,[14] the high reactivity of secondary chlorines in PCTFE indicates the ability of fluorine atoms to activate the chlorines toward atom transfer.

Graft Copolymerization of Styrene from P(VDF-*co*-CTFE). The ability of secondary chlorine in PCTFE oligomer to initiate ATRP can be used to prepare graft copolymers from commercial fluoropolymers containing CTFE units. In this work, commercial available copolymers of vinylidene fluoride and chlorotrifluoroethylene, P(VDF-*co*-CTFE), were used as macroinitiators to prepare graft copolymers via ATRP (Scheme 2).

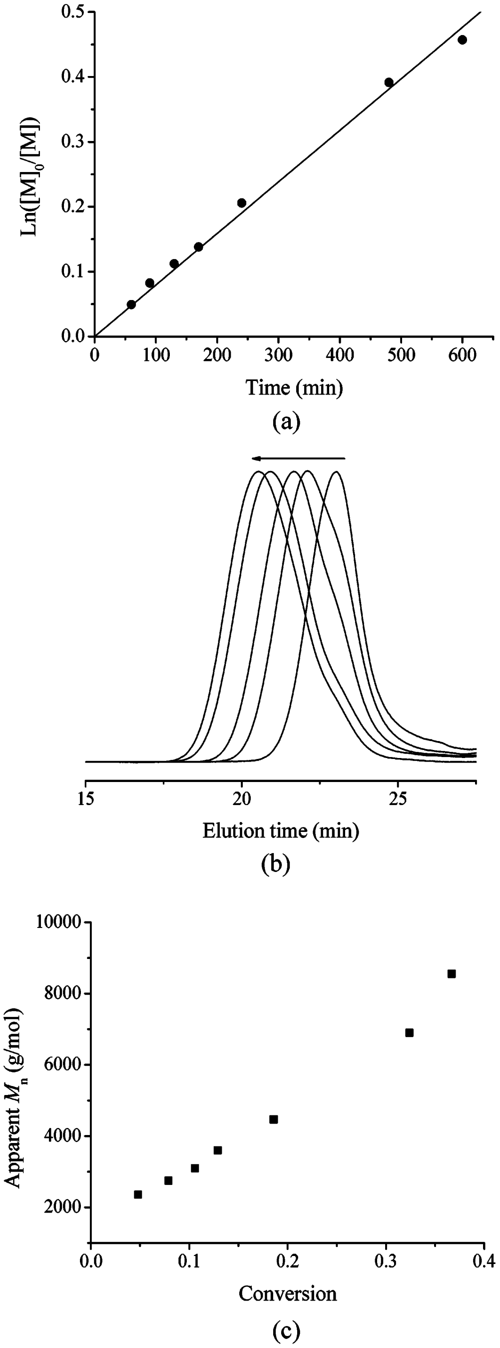
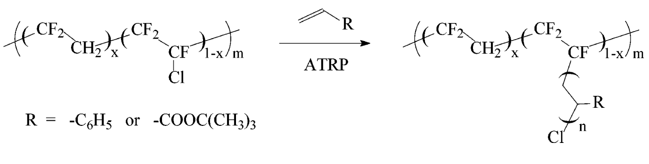


Figure 2. Homogeneous ATRP of styrene initiated by PCTFE oligomer at 120 °C (run 3, Table 2); $0.8[\mathrm{Cl}]_0 = 2[\mathrm{CuCl}]_0 = [\mathrm{BPy}]_0 = 0.01[\mathrm{styrene}]_0 = 0.0465$ M. (a) Semilogarithmic kinetics plot. (b) SEC traces of the resultant polymers at different polymerization times (from right to left: 60, 170, 240, 480, and 600 min). (c) The dependence of apparent number-average molecular weight (M_n) upon monomer conversion.

Scheme 2. Graft Copolymerization from P(VDF-*co*-CTFE) via ATRP



Two P(VDF-*co*-CTFE) copolymers, which contain 12.0 and 18.7 wt % of CTFE, respectively (as shown in Table 1), were used as macroinitiators. They have a pseudo-block structure, with a long VDF-rich block and a short CTFE-rich block. Thus, the initiating sites are densely distributed in the CTFE-rich block.

In the graft copolymerization from a macroinitiator with multiple initiating sites, the most critical aspect is cross-linking, which is caused by radical coupling. In ATRP the reversible deactivation of radicals to dormant species lowers the overall radical concentration significantly and, thus, minimizes irreversible terminations (like radical coupling), but the high local concentration of initiating sites along the macroinitiator still increases the possibility of cross-linking dramatically. So the experimental conditions for graft copolymerization should be optimized such that cross-linking is reduced as much as possible. It has been reported that by adding a radical deactivator (Cu(II)), terminating the polymerization at relatively low monomer conversion, and/or using solvents, the cross-linking during graft copolymerization can be suppressed significantly, and thus well-defined graft copolymers can be prepared.[10,11,20]

Since the macroinitiator, P(VDF-*co*-CTFE), is insoluble in the monomers used in this work (styrene, *tert*-butyl acrylate), polar solvents (such as DMF and NMP) were used to dissolve the macroinitiator. The addition of polar solvents also helped to dissolve the Cu(I) complex, ensuring a homogeneous reaction system.

Similar to the model reactions, when CuCl/PMDETA was used as catalyst for the graft copolymerization of styrene from P(VDF-*co*-CTFE) in solution, the reaction proceeded very rapidly. Actually, gelation (cross-linking) occurred instantly once the reaction flask was immersed in oil bath (run 1, Table 3). This is a clear indication of the high radical concentration and thus the high reactivity of the secondary chlorine in CTFE with respect to the radical generation under the polymerization conditions used.

When CuCl/BPy was used as catalyst, the graft copolymerization in solution was found to be a living process, indicated by the first-order polymerization kinetics (Figure 3a). SEC measurements showed that the initial negative refractive index signal (relative to solvent) of the macroinitiator changed to a positive one, and the molecular weight increased after the graft copolymerization, as shown in Figure 3b. In addition, the graft copolymers have strong UV absorption at 254 nm, while P(VDF-*co*-CTFE) has no absorption at this wavelength. The molecular weight distribution (MWD) of the resultant graft copolymer is bimodal, although its polydispersity is just slightly higher than that of the macroinitiator. To ensure the bimodality was not due to the existence of polystyrene homopolymer, which may form via thermal initiation,[21] the resultant copolymer was washed with cyclohexane. The SEC trace was virtually unchanged after washing. Instead, this bimodal distribution was likely a result of radical–radical coupling of chains during polymerization, which has been observed previously in ATRP graft copolymerizations.[4,10] Since the overall radical concentration was nearly constant (indicated by the first-order polymerization kinetics) and the resultant graft copolymer was still soluble, the extent of radical coupling must be negligible.

Because P(VDF-*co*-CTFE) is insoluble in $CDCl_3$, precipitation occurred when the initial kinetic sample was diluted with $CDCl_3$. During the graft copolymerization, the solubility of kinetic samples in $CDCl_3$ increased gradually, and eventually a clear solution could be obtained at relatively high monomer conversion. Provided that the content of grafted PS is high enough, the resultant graft copolymers can be dissolved in some solvents that are bad solvents for P(VDF-*co*-CTFE). For example, the graft copolymer from run 2 in Table 3 is soluble in THF, while P(VDF-*co*-CTFE) is insoluble in THF. This clearly indicates that the grafting of polystyrene improves the solubility of the parent fluoropolymer significantly.

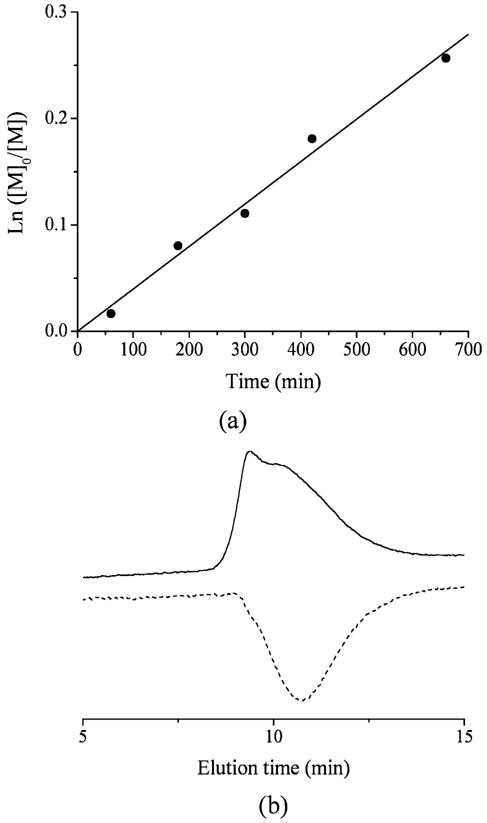


Figure 3. Graft copolymerization of styrene from P(VDF-*co*-CTFE)-31508 at 120 °C in NMP (run 4 in Table 3). (a) Semilogarithmic kinetics plot. (b) SEC traces of the resultant graft copolymer at the polymerization time of 12 h (solid line) and of the corresponding fluoropolymer, P(VDF-*co*-CTFE)-31508 (dashed line).

Since the secondary fluorine is also a potential ATRP initiator,[4] a control experiment was carried out to determine whether the secondary fluorine took part in the ATRP initiation during the graft copolymerization of styrene from P(VDF-*co*-CTFE). PVDF homopolymer (with the molecular weight of ~100 kg/mol) was used as macroinitiator for the control experiment under exactly the same reaction conditions as those used for run 2 in Table 3. The monomer conversion was quite similar in both cases. However, after washing the resultant polymer from the control experiment with THF, the SEC measurement showed that the residual polymer had exactly the same SEC trace as that of the starting PVDF, indicating that there was no appreciable initiation from the secondary fluorine for the ATRP of styrene in the control experiment. Instead, polystyrene homopolymer, which was dissolved in THF during washing, formed in run 3 (Table 3) due to the thermal initiation. The result of the control experiment indicates that the initiating efficiency of the secondary fluorine in PVDF is not high enough to polymerize styrene via ATRP under the reaction conditions we applied, although PVDF has been successfully used as macroinitiator to initiate the ATRP of methacrylates.[4] On the basis of the result from the control experiment, we can conclude that the graft copolymerizations from P(VDF-*co*-CTFE) were initiated from the secondary chlorines in the CTFE units exclusively.

The ^{1}H NMR spectra for P(VDF-*co*-CTFE) and P(VDF-*co*-CTFE)-*g*-PS are shown in Figure 4. The spectrum of P(VDF-*co*-CTFE) exhibits two peaks at 3.1 and 2.4 ppm, due to the well-known head-to-tail (ht) and head-to-head (hh) bonding arrangements of vinlyidene fluoride units, respectively. After the graft copolymerization of styrene, new peaks corresponding to polystyrene grafts appeared at 6.5−7.5 ppm (phenylic protons) and 1.3−2.2 ppm (methylene/methine protons), indicating the successful grafting of PS side chains.

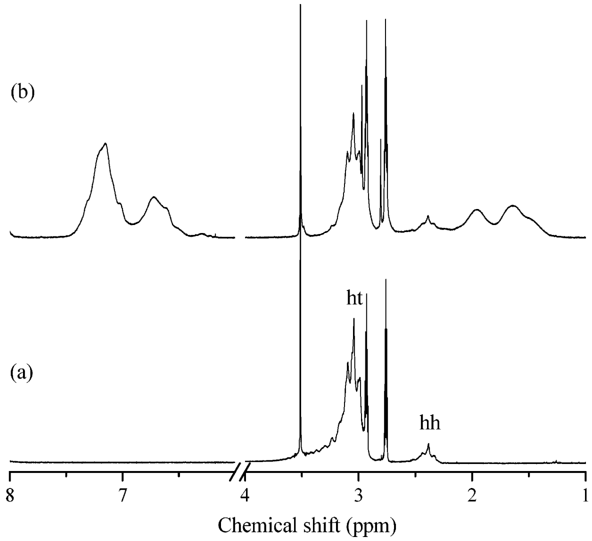


Figure 4. ^{1}H NMR spectra of (a) P(VDF-*co*-CTFE)-31008 and (b) P(VDF-*co*-CTFE)-*g*-PS (run 2, Table 3) in DMF-d_7. Resonances located at 2.75, 2.92, and 3.51 ppm are the solvent peaks.

Elemental analysis was used to determine the content of polystyrene side chains in the resultant graft copolymers. As shown in Table 3, both two graft copolymers contain more than 50 wt % of polystyrene, this is why they have much higher solubility than the parent fluoropolymer. The content of polystyrene in the graft copolymer determined by elemental analysis is in fairly good agreement with the calculated value based on the monomer conversion.

The resultant graft copolymers consist of a crystalline backbone and amorphous side chains. Thus, differential scanning calorimetry (DSC) was used to investigate their thermal properties and phase separation. Figure 5 shows DSC thermograms of P(VDF-*co*-CTFE)-31008 and the corresponding graft copolymer. The DSC thermogram of P(VDF-*co*-CTFE)-31008 shows a main melting peak at 167 °C with a shoulder at around 158 °C. The bimodal melting peak of P(VDF-*co*-CTFE) may be related to the presence of CTFE units in the copolymer, because pure PVDF showed a single melting peak at 163 °C under the same measurement conditions. After the grafting of PS side chains, in addition to the melting peak (T_m = 165 °C), a new transition temperature at 84 °C was observed, which should correspond to the glass transition of the PS graft. The existence of both the T_g of the PS graft and the T_m of the backbone indicates a microphase-separated morphology in this graft copolymer. Two characteristics were observed from the melting peak of the graft copolymer. First, a monomodal melting peak was observed, most probably due to the pseudo-block structure of the P(VDF-*co*-CTFE) and the selective grafting from the CTFE-rich block. The VDF-rich block of P(VDF-*co*-CTFE) remained almost intact after the graft copolymerization, and thus, the melting point of the resultant graft copolymer was very similar to the T_m of pure PVDF. Second, there was almost no melting point depression after graft copolymerization. In contrast, graft copolymers based on PVDF showed a melting point depression relative to the parent PVDF.[4] This again indicates that the grafting occurred solely from the secondary chlorines in the CTFE units, and the VDF units of the macroinitiator remained intact.

Atomic force microscopy (AFM) was used to characterize the thin film morphology of the macroinitiators and resultant

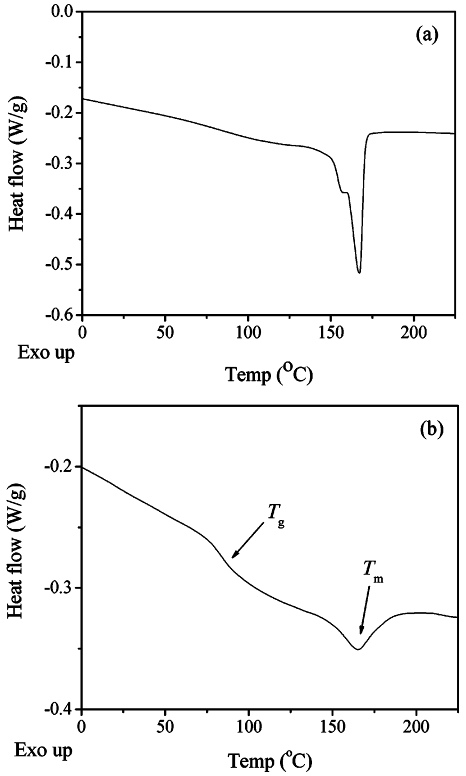


Figure 5. DSC thermograms upon heating at 10 °C/min for (a) P(VDF-*co*-CTFE)-31008 and (b) P(VDF-*co*-CTFE)-*g*-PS (run 2, Table 3).

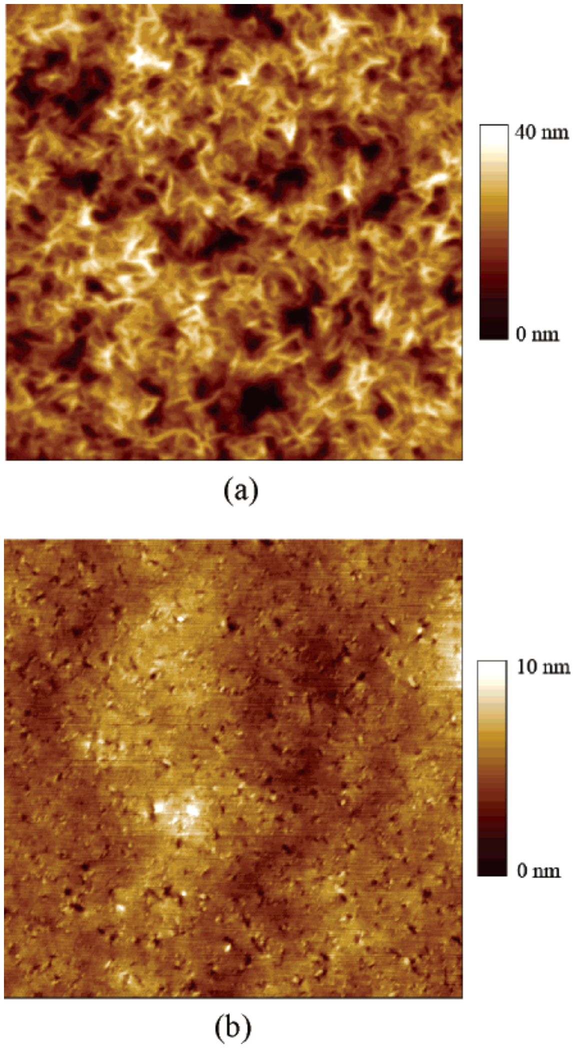


Figure 6. AFM height images (3 μm × 3 μm) of (a) P(VDF-*co*-CTFE)-31008 and (b) P(VDF-*co*-CTFE)-*g*-PS (run 2, Table 3) thin films on silicon wafer.

graft copolymers. As shown in Figure 6a, crystalline domains can be easily seen in the AFM image of P(VDF-*co*-CTFE), and the surface of film is relatively rough. Compared to the parent P(VDF-*co*-CTFE), thin film of the graft copolymer has a much smoother surface due to the dramatic decrease in crystallinity upon grafting (as revealed from the DSC measurements). The AFM image of the graft copolymer (Figure 6b) provides further evidence of the successful graft copolymerization, because macroscopic phase separation would have been observed if the resultant polymer is a mixture of P(VDF-*co*-CTFE) and PS homopolymer, due to the known incompatibility between PVDF and PS.[22] These graft copolymers could be of interest for modifying the compatibility between PVDF and PS by blending.

Graft Copolymerization of *tert*-Butyl Acrylate from P(VDF-*co*-CTFE). The strategy of graft copolymerization from P(VDF-*co*-CTFE) shown in Scheme 2 can be applied to other monomers, such as acrylates. In this work, *tert*-butyl acrylate (*t*BA) was chosen as the comonomer to grow poly(*tert*-butyl acrylate) (P*t*BA) grafts from P(VDF-*co*-CTFE), aiming to prepare amphiphilic graft copolymers via the hydrolysis of P*t*BA side chains.

Graft copolymerizations of *t*BA from P(VDF-*co*-CTFE) were carried out under different reaction conditions. At high polymerization temperatures (such as 100 °C), cross-linking (i.e., gelation) occurred within half an hour when CuCl/PMDETA was used as the catalyst system (run 1, Table 4). Lowering the radical concentration by decreasing the reaction temperature to 90 °C and adding a radical deactivator ($CuCl_2$), cross-linking was suppressed and a graft copolymer with relatively narrow molecular weight distribution was obtained (run 2, Table 4). The graft copolymerization proceeded very rapidly at 90 °C. After 45 min the reaction mixture became very viscous, and the polymerization was stopped to avoid cross-linking. Further lowering of the reaction temperature to 70 °C in the presence of $CuCl_2$ led to a much slower copolymerization (run 3, Table 4); however, the resultant graft copolymer still had a relatively narrow and monomodal molecular weight distribution. With increasing monomer conversion, the solubility of the graft copolymer in deuterated chloroform increased gradually. For example, in run 3 in Table 4, the kinetic sample at the reaction time of 20 h (conversion = 20.6%) was completely soluble in $CDCl_3$. This clearly indicates the successful graft copolymerization and the improvement of solubility upon grafting.

At relatively low reaction temperature (60−70 °C), the graft copolymerization could be carried out in a living manner without the addition of $CuCl_2$ (runs 4 and 5, Table 4). Figure 7 shows the SEC traces of a typical graft copolymer synthesized at 70 °C and the corresponding macroinitiator, P(VDF-*co*-CTFE)-31508. Similar to the grafting copolymerization of styrene, a positive peak was observed that shifted significantly to higher molecular weight relative to the parent fluoropolymer, indicating the successful grafting of P*t*BA side chains. Clearly, the molecular weight distribution for P(VDF-*co*-CTFE)-*g*-P*t*BA was monomodal, indicating the absence of coupling reactions.

The ^{1}H NMR spectrum of the resultant polymer provides further evidence for the graft copolymerization. After the formation of the graft copolymer with P*t*BA side chains, a characteristic strong peak at 1.5 ppm corresponding to methyl protons in *tert*-butyl group appeared, as shown in Figure 8b.

DSC was also used to investigate the thermal properties and phase separation of the graft copolymers with P*t*BA side chains.

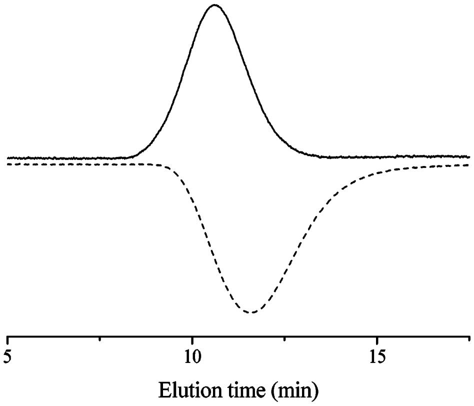


Figure 7. GPC traces of P(VDF-*co*-CTFE)-31508 (dashed line) and the graft copolymer (solid line) resulted from the polymerization of *t*BA at 70 °C in NMP for 1 h; [Cl]/[CuCl]/[PMDETA]/[*t*BA] = 1/0.8/0.8/41; V_S/V_M = 1.1/1 (run 4, Table 4).

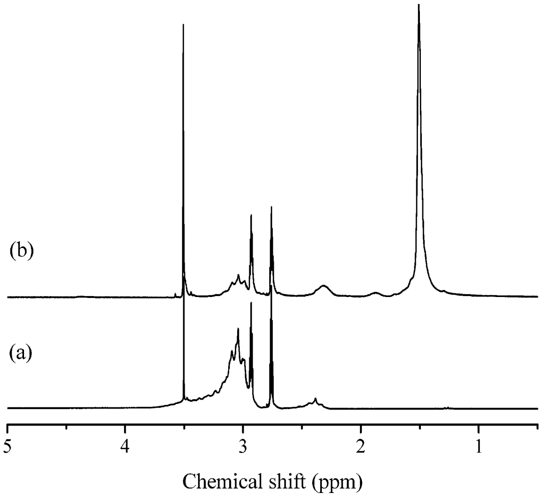


Figure 8. ^{1}H NMR spectra of (a) P(VDF-*co*-CTFE)-31508 and (b) P(VDF-*co*-CTFE)-*g*-P*t*BA (run 2, Table 4) in DMF-d_7.

Figure 9 shows the DSC thermograms of P(VDF-*co*-CTFE)-31508 and the corresponding graft copolymer with P*t*BA side chains. Very similar to P(VDF-*co*-CTFE)-31008, the DSC thermogram of P(VDF-*co*-CTFE)-31508 shows a main melting peak at 168 °C with a shoulder near 158 °C. After the grafting of P*t*BA side chains, a new transition temperature at 117 °C was observed, corresponding to the glass transition of P*t*BA grafts. The position of the melting peak of the resultant graft copolymer was almost the same as that of the main melting peak of the macroinitiator, again supporting the pseudo-block structure of the macroinitiator and the selective grafting from the CTFE-rich block. The existence of both the T_g of the P*t*BA grafts and the T_m of the backbone indicates a microphase-separated morphology in this graft copolymer.

Preparation of Amphiphilic Graft Copolymer Based on P(VDF-*co*-CTFE). It is well-known that P*t*BA can be easily converted to poly(acrylic acid) (PAA) via hydrolysis. So amphiphilic graft copolymers with PAA side chains, P(VDF-*co*-CTFE)-*g*-PAA, can be synthesized from the precursor graft copolymers, P(VDF-*co*-CTFE)-*g*-P*t*BA. Acidic hydrolysis of P*t*BA grafts was carried out in NMP at 100 °C for 2 days. ^{1}H NMR measurements showed that complete hydrolysis was achieved, as indicated by the disappearance of methyl protons in *tert*-butyl group at 1.5 ppm (Figure 10b).

Amphiphilic graft copolymers with hydrophobic fluorinated backbone and hydrophilic grafts have many important applications. A good example is that graft copolymers with PVDF backbone and poly(methacrylic acid) (PMAA) grafts have been used to prepare membranes with pH-sensitive separation characteristics.[16] One can expect similar applications for the graft copolymers with P(VDF-*co*-CTFE) backbone and PAA side chains. Different from PVDF-*g*-PMAA used in ref 16, which has very low grafting density, dense grafting can be achieved when P(VDF-*co*-CTFE) is used as macroinitiator. This may increases the permeability of fabricated membranes to aqueous solutions considerably.

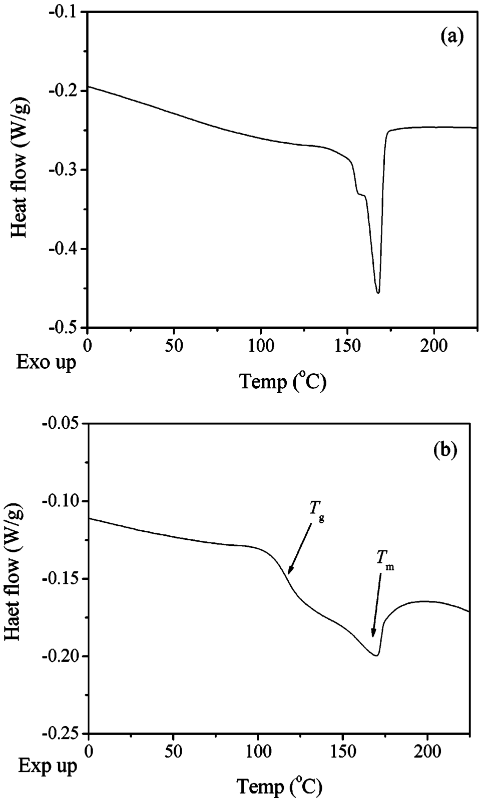


Figure 9. DSC thermograms upon heating at 10 °C/min for (a) P(VDF-*co*-CTFE)-31508 and (b) P(VDF-*co*-CTFE)-*g*- P*t*BA (run 3, Table 4).

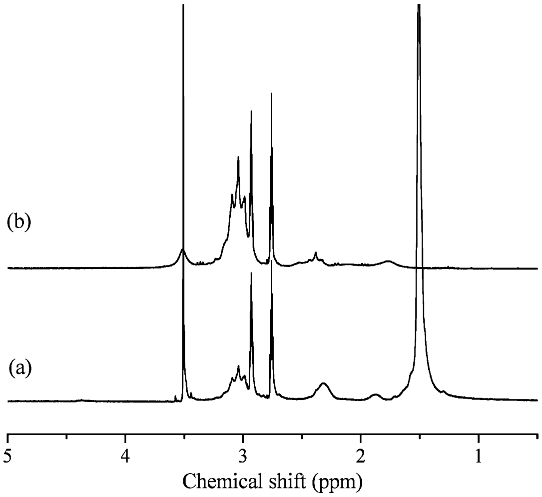


Figure 10. ^{1}H NMR spectra of P(VDF-*co*-CTFE)-*g*-P*t*BA (run 2, Table 4) (a) and its hydrolysis product P(VDF-*co*-CTFE)-*g*-PAA (b) in DMF-d_7.

Conclusions

In summary, the secondary chlorines in CTFE units of fluoropolymers were found to be able to initiate ATRP of various monomers. A convenient method, based on the graft copolymerization of comonomers from fluoropolymers containing CTFE units via ATRP, has been developed and used to modify some important commercial fluoropolymers, such as P(VDF-*co*-CTFE). Various polymers (PS, P*t*BA) have been grafted from P(VDF-*co*-CTFE), resulting in graft copolymers with improved solubility and phase compatibility. Hydrolysis of P*t*BA grafts of P(VDF-*co*-CTFE)-*g*-P*t*BA resulted in amphiphilic graft copolymers with PAA side chains, which may find potential applications in the fabrication of pH-sensitive membranes. Because of the selective grafting from the secondary chlorine in CTFE unit, the grafting density as well as the distribution of grafts solely depends on the density and distribution of CTFE units in the parent fluoropolymers.

Various fluoro-copolymers containing CTFE units are commercially available and have been widely used in the manufacture of many products due to their high mechanical strength and excellent thermal and chemical stability. These fluoropolymers have very different structures, such as alternating (copolymers of chlorotrifluoroethylene with alkyl vinyl ether), pseudo-block (P(VDF-*co*-CTFE)), gradient, and so forth. On the basis of these fluoropolymers, we will be able to prepare graft copolymers with desired structures and favorable properties. Preparation of graft copolymers using other CTFE-containing fluoropolymers is undergoing, and the results will be published elsewhere.

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Supporting Information Available: Mass spectrum and ^{13}C NMR spectrum of poly(chlorotrifluoroethylene) (PCTFE) oligomer. This material is available free of charge via the Internet at http://pubs.acs.org.

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