Synthesis of Poly(vinylidene fluoride)-*b*-poly(styrene sulfonate) Block Copolymers by Controlled Radical Polymerizations

Gaël Laruelle,[1] Erwan Nicol,[1] Bruno Ameduri,[2] Jean-François Tassin,[1] Noureddine Ajellal[2]

[1]Polymères, Colloïdes, Interfaces, UMR CNRS 6120, Université du Maine, 72085 Le Mans Cedex 9, France
[2]Engineering and Macromolecular Architectures, Institut Charles Gerhardt UMR (CNRS) 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 34296 Montpellier Cedex 1, France

Correspondence to: E. Nicol (E-mail: erwan.nicol@univ-lemans.fr) or B. Ameduri (E-mail: bruno.ameduri@enscm.fr)

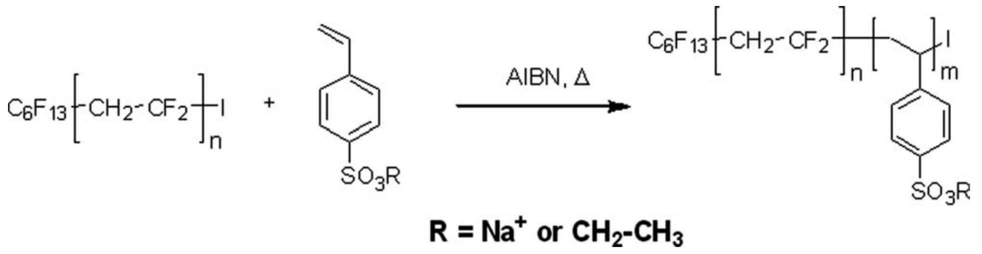
Received 20 January 2011; accepted 15 June 2011; published online 7 July 2011
DOI: 10.1002/pola.24836

ABSTRACT: Block copolymers based on poly(vinylidene fluoride), PVDF, and a series of poly(aromatic sulfonate) sequences were synthesized from controlled radical polymerizations (CRPs). According to the aromatic monomers, appropriate techniques of CRP were chosen: either iodine transfer polymerization (ITP) or atom transfer radical polymerization (ATRP) from PVDF-I macromolecular chain transfer agents (CTAs) or PVDF-CCl_3 macroinitiator, respectively. These precursors were produced either by ITP of VDF with $C_6F_{13}I$ or by radical telomerization of VDF with chloroform, respectively. Poly(vinylidene fluoride)-*b*-poly(sodium styrene sulfonate), PVDF-*b*-PSSS, block copolymers were produced from both techniques via a direct polymerization of sodium styrene sulfonate (SSS) monomer or an indirect way with the use of styrene sulfonate ethyl ester (SSE) as a protected monomer. Although the reaction led to block copolymers, the kinetics of ITP of SSS showed that PVDF-I macromolecular CTAs were not totally efficient because a limitation of the CTA consumption (56%) was observed. This was probably explained by both the low activity of the CTA (that contained inefficient PVDF-CF_2CH_2—I) and a fast propagation rate of the monomer. That behavior was also noted in the ITP of SSE. On the other hand, ATRP of SSS initiated by PVDF-CCl_3 was more controlled up to 50% of conversion leading to PVDF-*b*-PSSS block copolymer with an average number molar mass of 6000 g·mol^{-1}. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3960–3969, 2011

KEYWORDS: atom transfer radical polymerization (ATRP); block copolymers; fluoropolymers; iodine transfer polymerization (ITP); poly(styrene sulfonate); poly(vinylidene fluoride) (PVDF)

INTRODUCTION In the field of proton-conducting materials, fluorinated polymers that bear sulfonated groups are frequently used. The best example deals with the sulfonated tetrafluoroethylene copolymer discovered by DuPont de Nemours in 1968 and marketed by this company under the Nafion® trademark. Numerous works have been achieved to find out alternatives to Nafion® membranes in proton exchange membrane fuel cells. One of the explored ways concerns the blending of poly(vinylidene fluoride) (PVDF) with sulfonated polymers.[1,2] Moszczynski et al.[3] processed interpenetrated polymer networks by polymerizing *in situ* styrene sulfonic acid (SSA) in a porous poly(vinylidene fluoride-*co*-hexafluoropropylene) copolymeric membrane. However, the proton conductivity drops after a few days of utilization because of the elution of poly(styrene sulfonic acid) in water. Piboonsatsanasakul et al.[4] investigated PVDF/sulfonated PS (SPS) blends using PS-*b*-PMMA block copolymers as compatibilizers. The PMMA segment was compatible with PVDF and the PS block was compatible with the SPS phase. The compatibilization reduced the methanol permeability and reduced the size of the microdomains (hence improving the mechanical properties).

To improve the compatibilization of PVDF- and poly(styrene sulfonate) (PSS)-based materials, it was worth investigating the synthesis of PVDF-*b*-PSS diblock copolymers. Block copolymers exhibit very interesting properties in the bulk and in solution because of their ambivalent character.[5,6] One of the applications of block copolymers is their use as compatibilizers for polymer blends. When smartly chosen, they are known to reduce the interfacial tension between both components of the blend and to prevent the droplets coalescence.[7] However, the synthesis of structures made of repeating units that have very different polarities can be a real challenge. The development of controlled radical polymerization (CRP) techniques[8] has considerably increased the versatile number of block copolymers potentially synthesizable. The synthesis of block copolymers based on PVDF or poly(VDF-*co*-HFP) copolymer has already been reported in the literature,[9] either using iodine transfer polymerization (ITP),[10] atom transfer radical polymerization (ATRP) techniques,[11–14] or macromolecular design as interchange of xanthate.[15] Recently, Elabd and Hickner[16] reviewed the role that ion-containing block copolymers could play in the next



SCHEME 1 Iodine transfer polymerization (ITP) of styrene sulfonate derivatives in the presence of PVDF-I chain transfer agent (CTA).

generation of proton exchange membranes. The importance of aryl sulfonic acid groups, in such proton-conducting materials based on block copolymer, is clearly highlighted. Poly(VDF-*co*-HFP)-*b*-sulfonated polystyrene was synthesized and studied by Holdcroft's group.[17,18] In a first step, this team polymerized a PS block by ATRP from a poly(VDF-*co*-HFP) macroinitiator. Then, the PS block (SPS) was sulfonated using acetyl sulfate. Xu et al.[14] used a similar strategy to elaborate SPS-*b*-PVDF-*b*-SPS triblock copolymers. A chain-end-functionalized PVDF was synthesized by radical polymerization using 4-chloromethyl benzoyl peroxide as an initiator. The ATRP of styrene was initiated by this macroinitiator to generate a PS-*b*-PVDF-*b*-PS triblock copolymer that was postsulfonated using chlorosulfonic acid. This method was efficient but required two synthesis steps.

To the best of our knowledge, the literature does not report any direct synthesis of PVDF-*b*-poly(sodium styrene sulfonate) (PSSS) using CRP. However, both monomers can be polymerized by these techniques. VDF has been successfully polymerized by ITP.[19,20] PSSS can be synthesized by nitroxide-mediated polymerization (NMP),[21] by reversible addition-fragmentation chain-transfer,[22] or by ATRP.[23,24] This last technique was applied to synthesize block copolymers[25] or for growing PSSS chains from organic[26,27] or inorganic surfaces.[28–32] It was of interest to investigate the synthesis of PVDF-*b*-PSS block copolymers. This is the objective of this article that describes the elaboration of PDVF-*b*-PSS from PVDF macroinitiators via two CRP techniques (ITP and ATRP) of styrene sulfonate.

RESULTS AND DISCUSSION

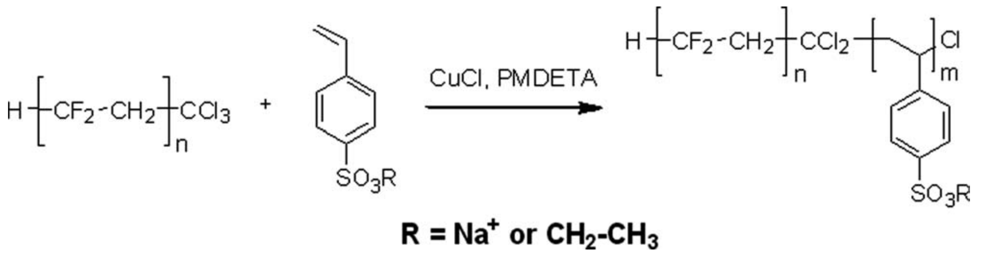
The aim of this work is the synthesis of block copolymers composed of vinylidene fluoride units and styrene sulfonate units. For the formation of the PSS block, the direct polymerization of the sodium styrene sulfonate (SSS) monomer via two types of functional PVDF was first considered. Functional PVDF can be synthesized by several techniques such as telomerization[33] and ITP.[34] According to the technique and to the transfer agent used, the resulting PVDF can be functionalized either by an iodine atom or by a $-CCl_3$ end group. Both types of functionalized PVDF can act as macrotransfer agent for the ITP (Scheme 1) or as a macroinitiator in an ATRP (Scheme 2) of styrene sulfonate derivatives, respectively, leading to the formation of diblock copolymers.

ITP of Styrene Sulfonate Monomers in the Presence of ω-Iodofluorinated Chain Transfer Agents

ITP of SSS from $C_6F_{13}I$

Several attempts of ITP of SSS with $C_6F_{13}I$ as a chain transfer agent (CTA) were carried out. This transfer agent was chosen because it was supposed to be a model molecule that can mimic the behavior of PVDF-I macrotransfer agents. For example, this perfluoroalkyl iodide was used by David et al.[35] in the ITP of vinyl phosphonic acid. However, chemical natures and solubilities of $C_6F_{13}I$ and PVDF-I are different that could lead to different reactivities.

ITP of SSS was carried out in a mixture of *N*,*N*-dimethylformamide (DMF) and water (80/20 v/v) at 70 °C in the presence of $C_6F_{13}I$ and AIBN as the transfer agent and the radical initiator, respectively. The reactant molar ratios were $[SSS]_0$:$[C_6F_{13}I]_0$:$[AIBN]_0 = 20{:}1{:}0.2$ for a monomer concentration $[SSS]_0 = 0.6$ mol·L^{-1}. Proton NMR proved that the monomer was consumed, but ^{19}F NMR, performed on the final purified polymer, indicated the absence of the transfer agent at the chains ends. The evolution of molecular weights (assessed by size exclusion chromatography (SEC) in water) with the conversion was almost constant ($M_n = 4200$ g·mol^{-1}, poly(ethylene oxide) standards), and the polydispersity index remained high (PDI = 4.2). Hence, it was



SCHEME 2 Atom transfer radical polymerization (ATRP) of styrene sulfonate derivatives initiated by PVDF-CCl_3 macroinitiator.

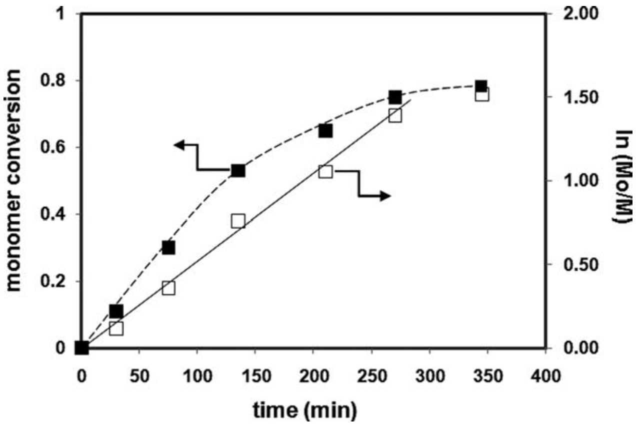


FIGURE 1 Kinetics plots, SSS conversion, and ln$[M]_0/[M]$ versus as a function of time, for iodine transfer polymerization of SSS initiated by AIBN in the presence of C_6F_{13}-$(VDF)_6$-I as the macromolecular chain transfer agent. Conditions: $[SSS]_0$:$[PVDF\text{-}CF_2I]_0$:$[AIBN]_0$ = 28:1:0.2 (—CF_2I functionality = 0.31), DMSO, 70 °C.

concluded that the transfer agent did not play its role notably because of a bad compatibility with the hydrophilic monomer. The polymerization only occurred via a conventional radical polymerization process initiated by AIBN. Attempts performed in other solvents (pure DMF and dimethylsulfoxide) led to the same results.

ITP of SSS from PVDF-I

Despite the noneffectiveness of the ITP of SSS in the presence of $C_6F_{13}I$, the polymerization of SSS was attempted from PVDF-I. Because $C_6F_{13}I$ and PVDF-I are chemically different, their efficiency as a CTA could, as well, be different. Valade et al.[10] reported the synthesis of poly(vinylidene fluoride)-*block*-poly(styrene) (PVDF-*b*-PS) from the ITP of styrene in the presence of PVDF-I. The same macromolecular CTA was used for the copolymerization of PVDF with SSS. ITP of SSS was initiated by AIBN in DMSO at 70 °C, in the presence of C_6F_{13}-$(VDF)_6$-I as the CTA. The CF_2—I functionality of this polymer was estimated to 31%. The following molar ratio was used: $[SSS]_0$:$[PVDF\text{-}CF_2I]_0$:$[AIBN]_0$ = 28:1:0.2 for a monomer concentration $[SSS]_0 = 1.2$ mol·L^{-1}. Aliquots were frequently withdrawn to monitor the evolution of the monomer conversion by ^1H NMR spectroscopy by comparing the integrals of the ethylenic protons (at 5.27, 5.84, and 6.73 ppm) with those of the aromatic ones (between 6.2 and 7.8 ppm). Figure 1 exhibits the kinetic plot of this ITP.

The evolution of ln($[M]_0/[M]$) versus time is quasilinear up to 70% SSS conversion. In this range of conversion, the reaction follows a first-order kinetics indicating a constant concentration of radicals. After 70% conversion, termination reactions seemed to occur. A linear evolution of the molecular weight versus monomer conversion would be the only clear evidence of the controlled character of the polymerization. However, the molecular weights and the PDI of the resulting copolymers could not be assessed because the copolymers formed were not soluble in usual solvents of the SEC (THF, DMF, water…). Nevertheless, the efficiency of the macromolecular transfer agent was checked by ^{19}F NMR spectroscopy (Fig. 2). Before polymerization, this spectrum exhibits all the peaks assigned to VDF backbone (peak d) and to the chain ends (C_6F_{13} on one hand (signals a, b, and c) and CH_2—CF_2—I on the other hand (peak e)). Additional e′ signal arises from the presence of a second type of PVDF chains that bears a CF_2—CH_2—I end group.[10,18] Indeed, during ITP of VDF, two kinds of VDF-I end groups were generated. This second type of PVDF-I was demonstrated to be nonactive in ITP.[10,19,36] Thus, in a further step, this signal is expected to remain unchanged. After polymerization [Fig. 2(b)], the presence of e signal at the same chemical shift indicates that a nonnegligible amount of PVDF-CH_2—CF_2—I did not react during ITP of SSS. However, a small additional signal attributed to the perfluoromethylene group linked to the first SSS unit appeared at −93 ppm. From the integral of this signal before and after ITP of SSS, 56% of the PVDF-CH_2—CF_2—I really acted as a transfer agent during the ITP

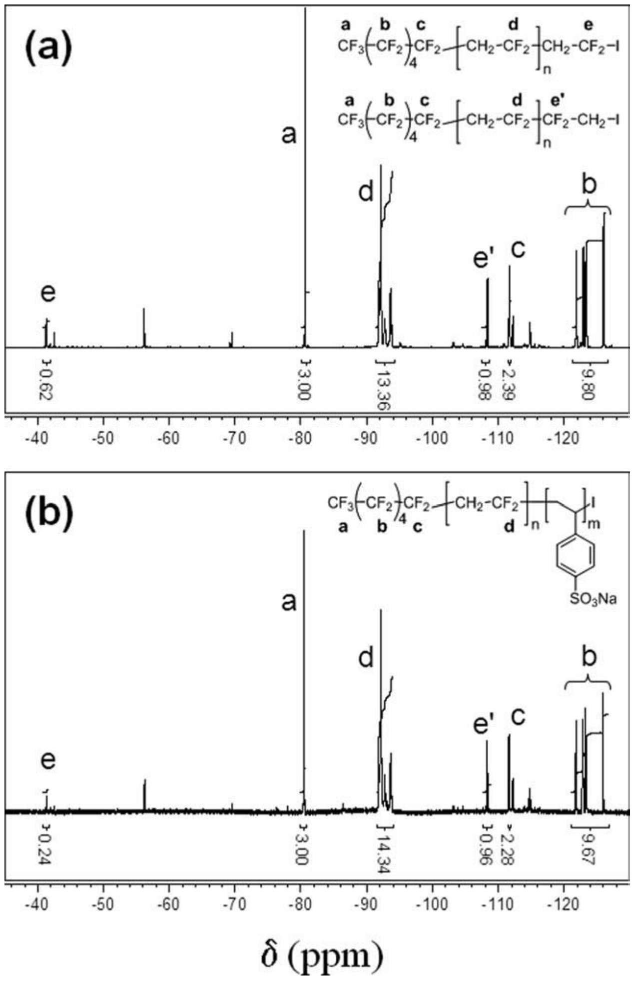


FIGURE 2 ^{19}F NMR spectra recorded in DMSO-d_6 of C_6F_{13}-$(VDF)_6$-I (functionality of —CF_2I = 0.31) macrotransfer agent (top) and the purified product after ITP of sodium styrene sulfonate (bottom).

for 80% of SSS conversion. This efficiency is low in comparison with the value obtained by Valade et al.[10] during ITP of styrene from PVDF-I in acetonitrile 70 °C (consumption of 80% of CTA for 80% conversion of styrene). Proton NMR performed on this sample gave an integral ratio of the aromatic signal of PSSS with respect to the CH_2 signal of PVDF (centered at 2.9 ppm) of 7.4. Assuming that only 31% of the CTA was CF_2—I functionalized and that only 56% of the PVDF-CH_2—CF_2—I were involved in the copolymerization, a degree of polymerization of 128 was found for SSS block. This value is higher than the theoretical targeted degree of polymerization ($DP_{th} = 22.4$) confirming the low efficiency of the transfer agent.

As the direct polymerization of SSS led to unsatisfying results (low activity of the PVDF-I), it was worth using a nonionic monomer precursor such as styrene sulfonate ethyl ester (SSE). The elaboration of PSS is often carried out by sulfonation of PS.[37,38] However, various authors have recently reported the advantages of polymerizing styrene sulfonate ester over the sulfonation way.[25,39–41] This method avoids incomplete and random sulfonation, crosslinking,[42] and degradation, which may occur in the sulfonation of PS.

ITP of SSE in the Presence of $C_6F_{13}I$

Before using VDF-I as the macromolecular transfer agent for ITP of SSE, the ITP of SSE with $C_6F_{13}I$ was investigated. The polymerization of SSE was carried out in DMF at 70 °C in the presence of $C_6F_{13}I$ and AIBN using the following concentrations ratio: $[SSE]_0:[C_6F_{13}I]_0:[AIBN]_0 = 30:1:0.2$ for a monomer concentration $[SSE]_0 = 3\ \text{mol}\cdot L^{-1}$. The evolution of the monomer conversion was monitored by injecting withdrawn samples in gas chromatography (GC).

Kinetic plot [Fig. 3(a)] shows a linear dependence of $\ln([M]_0/[M])$ versus time as observed for ITP of SSE with $C_6F_{13}I$. This linearity arises from a constant concentration of radicals through the polymerization. SEC was performed in THF on homopolymers generated during the ITP. The evolutions of the number-average molar masses and polydispersity indices with conversion are displayed in Figure 3(b). The decrease of molar mass versus conversion is characteristic of a conventional radical telomerization reaction.[33,43] As previously demonstrated,[44,45] the evolution of the number-average molar mass with monomer conversion, in the case of telomerization reaction, can be predicted by the following equation:

$$\overline{M_n} = \left(p.[M]_0.M_{\text{monomer}}\right)/\left([CTA]_0.[1-(1-p)^{C_{Tr}}]\right), \tag{1}$$

where $[M]_0$, M_{monomer} $[CTA]_0$, p, and C_{Tr} stand for the initial monomer concentration, the molar mass of the monomer, the initial CTA concentration, the conversion, and the transfer constant of the CTA ($C_{Tr} = k_{Tr}/k_p$), respectively.

If the ITP was controlled, a linear increase of the M_n with the conversion would be expected. In our case, M_n decreases with the conversion and the polydispersity indices remained low (1.2–1.4). This behavior is generally observed for $C_{Tr} < 1$. In that case, the CTA consumption is slow and the experimental molecular weights should decrease as the reaction proceeds, hence leading to broader polydispersity indices. David et al.[35] observed this behavior for ITP of vinyl phosphonic acid with the same alkyl iodide transfer agent, but in their case C_{Tr} was 4.3 at 80 °C. A C_{Tr} value higher than 1 (at 80 °C) generally means a pseudo-living/controlled system, so they explained this behavior by a very low k_p.

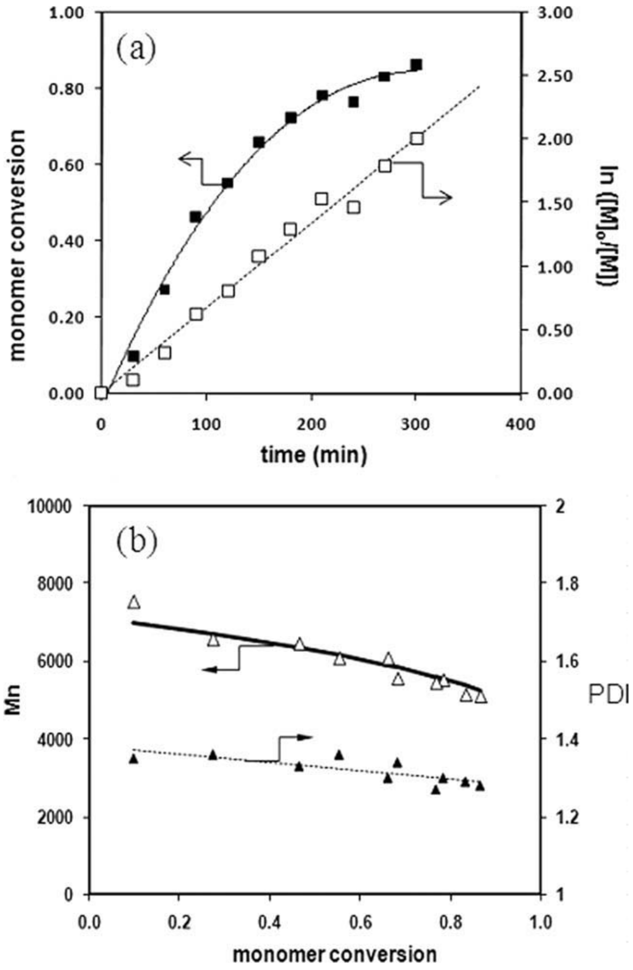


FIGURE 3 (a) Time dependence of monomer conversion (filled squares) and $\ln[M]_0/[M]$ (open squares) for iodine transfer polymerization of styrene sulfonate ethyl ester in the presence of $C_6F_{13}I$. (b) M_n (with PS standards)(open triangles) and polydispersity index (PDI)(filled triangles) versus SSE conversion for iodine transfer polymerization of SSE initiated with AIBN in the presence of $C_6F_{13}I$ as the chain transfer agent. Full line is a fit to M_n data according to eq 1 for a C_{Tr} value of 0.6. Conditions: $[SSE]_0:[C_6F_{13}I]_0:[AIBN]_0 = 30:1:0.2$, acetonitrile, 70 °C.

A method for assessing C_{Tr} is based on the evolution of M_n or DP_n versus monomer conversion. This method uses eq 1 derived from the Boutevin et al.'s law[44] established for the telomerization process. The evolution of M_n versus conversion was fitted according to this equation by varying the C_{Tr} value. A good fit was obtained for a value of C_{Tr} at 70 °C equal to 0.6 (Fig. 3), but it must be pointed out that the M_n

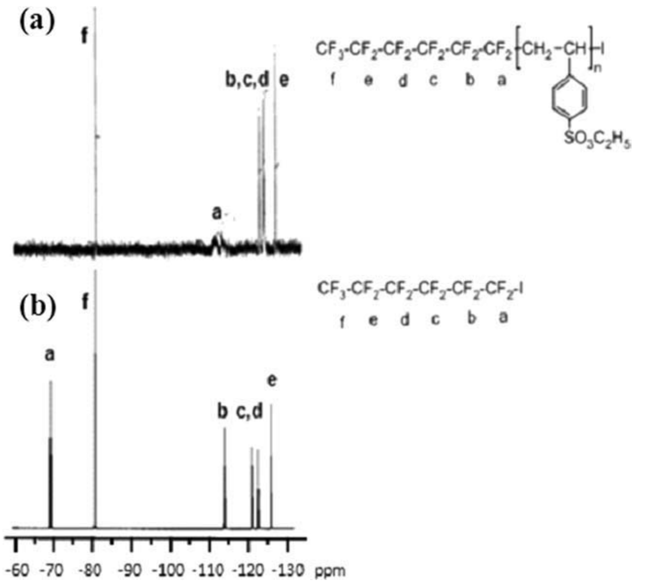


FIGURE 4 ^{19}F NMR spectrum (recorded in DMSO-d_6) of poly(styrene sulfonate ethyl ester) synthesized by iodine transfer polymerization of SSE initiated with AIBN in the presence of $C_6F_{13}I$ as the chain transfer agent (top spectrum: a), ^{19}F NMR spectrum (recorded in DMSO-d_6) of $C_6F_{13}I$ (bottom spectrum: b).

values were given in PS equivalent and, thus, were not absolute ones. Several fits attempted by shifting up or down the M_n values and C_{Tr} values ranging between 0.3 and 0.7 (at 70 °C) were obtained. Thus, it can be assumed that the C_{Tr} value is below 1 as expected for a radical telomerization.[33]

After the polymerization, the purified polymer was characterized by ^{19}F NMR (Fig. 4) to check the presence of the alkyl iodide transfer agent. The signal centered at −69 ppm is characteristic of the CF_2—I bond of the perfluoroalkyl transfer agent (Fig. 4, bottom spectrum: b). It disappears after polymerization evidencing the formation of C_6F_{13}-PSSE polymer. At the same time, CF_2 in the β position of the iodine atom undergoes at high field shift from −113 to −122 ppm (Fig. 4, top spectrum: a). These results confirm the effectiveness of the ITP of SSE.

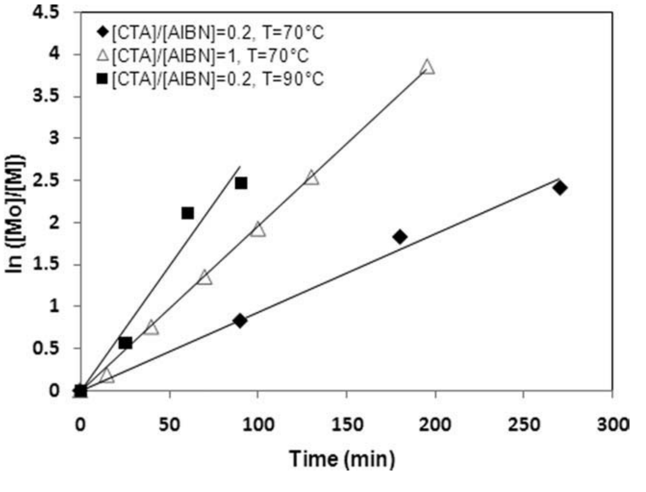


FIGURE 5 ln[M]$_0$/[M] versus time for iodine transfer polymerization of styrene sulfonate ethyl ester (SSE) initiated with AIBN in the presence of $C_6F_{13}(VDF)_{20}$-I as the macromolecular chain transfer agent performed in DMF. Conditions: ◆ $[SSE]_0$:$[C_6F_{13}(VDF)_{20}\text{-}I]_0$:$[AIBN]_0$ = 30:1:0.2 and T = 70 °C, △ $[SSE]_0$:$[C_6F_{13}(VDF)_{20}\text{-}I]_0$:$[AIBN]_0$ = 30:1:1 and T = 70 °C, ■ $[SSE]_0$:$[C_6F_{13}(VDF)_{20}\text{-}I]_0$:$[AIBN]_0$ = 30:1:0.2 and T = 90 °C.

ITP of SSE from PVDF-I

ITP of SSE was performed in DMF at 70 and 90 °C in the presence of $C_6F_{13}(VDF)_{20}$-I (containing 42% of CF_2—I chain ends), AIBN and 1,2-dimethoxybenzene (as the internal standard), keeping the $[M]_0/[AIBN]_0$ ratio constant ($[M]_0/[AIBN]_0$=125), and varying $[CTA]_0/[AIBN]_0$ ratio from 0.2 to 1. The initial SSE concentration was 3 mol·L^{-1}. Aliquots were frequently sampled and injected in GC to monitor the evolution of the monomer conversion thanks to the presence of the internal standard. Figure 5 shows the kinetic plots of such a polymerization. The characteristic first order is evidenced indicating a constant concentration of radicals.

The efficiency of the macromolecular CTA could be evidenced from the ^{19}F NMR spectrum shown in Figure 6. The

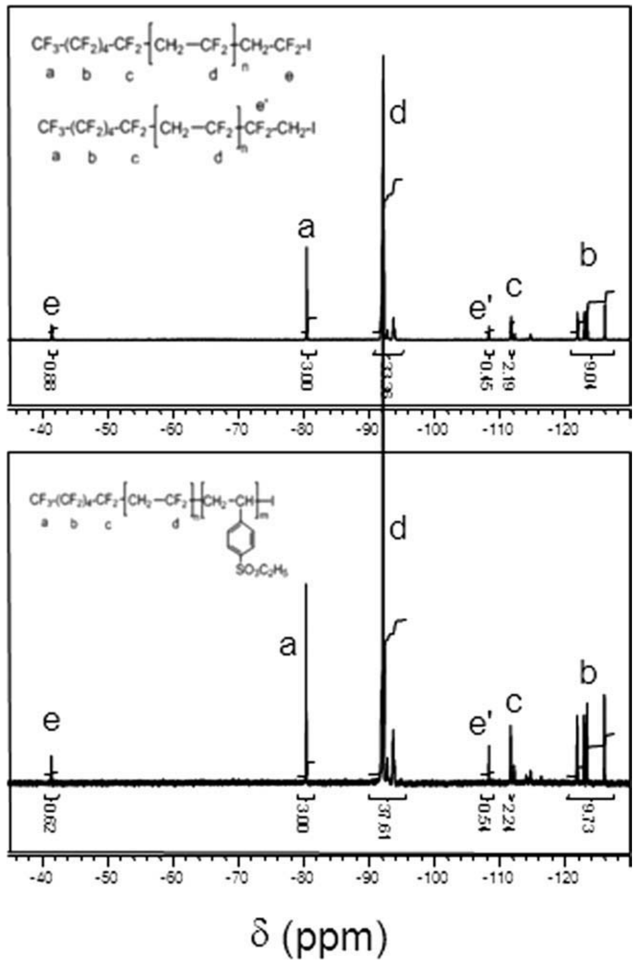


FIGURE 6 ^{19}F NMR spectra (recorded in DMSO-d_6) of C_6F_{13}-$(VDF)_{20}$-I macromolecular CTA (CF_2-I functionality = 0.42) (top) and the final product after ITP of SSE (bottom).

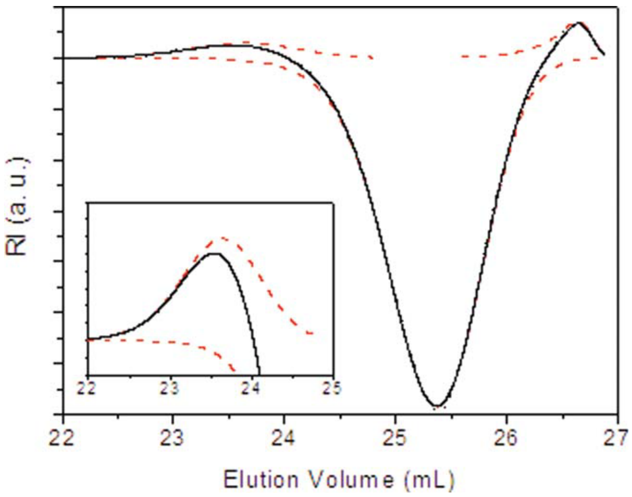


FIGURE 7 SEC trace (in NMP + 10^{-1} M LiBr) of the total products mixture obtained by ITP of SSE in the presence C_6F_{13}-$(VDF)_{20}$-I as macromolecular CTA. Dashed lines are the deconvolutions of the signal. Inset represents an expansion of the 22–25 mL zone of the signal of the copolymer.

same analysis as that previously described for ITP of SSS can be made. By integrating the e signal (CH_2—CF_2—I: functionality = 42%) before and after ITP of SSE, the amount of unreacted PVDF-CH_2—CF_2—I can be assessed. At 70 °C and for a $[CTA]_0/[I]_0 = 0.2$, one can estimate at the end of the polymerization (for a monomer conversion of 90%) that only 30% of PVDF-CH_2—CF_2—I reacts during the ITP of SSE. This value is lower than those obtained for ITP of SSS. Increasing the $[CTA]_0/[I]_0$ ratio or the temperature did not improve the transfer efficiency. Furthermore, ^1H NMR spectrum indicated a loss of around 80% of the ethyl moieties borne by styrene sulfonate groups.

The resulting material was characterized by SEC in *N*-methylpyrrolidone (NMP) containing 10^{-1} M of LiBr. SEC trace of the sample obtained by ITP of SSE from C_6F_{13}-$(VDF)_{20}$-I as the macromolecular CTA (Fig. 7) exhibits two peaks of opposite refractometric responses corresponding to the C_6F_{13}-$(VDF)_{20}$-I precursor (that led to a negative signal) and to PVDF-*b*-PSSE copolymer (positive signal). The low intensity of the copolymer signal can be partially explained by the very low value of d*n*/d*C* for PVDF-*b*-PSSE copolymers in NMP (not measured accurately). Indeed, d*n*/d*C* values are -0.05 mL·g^{-1} for the PDVF and 0.053 mL·g^{-1} for the PSSS leading to a d*n*/d*C* close to 0 for a 50/50 (w/w) block copolymer. The analysis of the copolymer trace gave average molar masses $M_n = 8600$ g·mol^{-1} and $M_w = 10{,}100$ g·mol^{-1} (PS standards) (PDI = 1.17). Thus, although side reactions (not clearly identified yet) involving the ethyl sulfonate group occurred, the polydispersity of the block copolymer remained low, indicating that the control over the polymerization was not completely lost. However, the moderate efficiency of the macromolecular transfer agent remained an issue.

ATRP of Styrene Sulfonate Monomers Initiated by PVDF-CCl_3

PVDF-*b*-PSSS block copolymers can be prepared by ITP using PVDF-I as the CTA via direct polymerization. However, PVDF-I did not completely react (as PVDF-CH_2—I is unreactive while a limited amount of PVDF-CF_2—I reacted) leading to a mixture of PVDF-*b*-PSSS and unreacted PVDF, which were difficult to separate. This can be a drawback for further applications. Hence, another way of preparing block copolymers was investigated. ATRP of SSS was attempted using PVDF-CCl_3 as a macroinitiator. PVDF-CCl_3 was prepared by radical telomerization of VDF with chloroform,[46] and, for this reactants, only one type of PVDF was generated in contrast to PVDF-I obtained by ITP. Therefore, in the case of successful ATRP of SSS, PVDF-*b*-PSSS block copolymers free of unreacted PVDF will be obtained.

We were inspired by Destarac et al.'s work[11] who used α-trichloromethylated VDF telomers (H-$(VDF)_n$-CCl_3) as ATRP initiators for synthesizing PVDF-based block copolymers involving PS, poly(acrylate), and poly(methacrylate) blocks. In this study, similar α-trichloromethylated VDF telomers were used as the macroinitators in ATRPs of SSS and SSE that have never been reported (Scheme 2).

Direct ATRP of SSS from PVDF-CCl_3

ATRP was carried out in DMSO at 80 °C with $PVDF_{46}$-CCl_3 or $PVDF_{19}$-CCl_3 as macroinitiator catalyzed by a CuCl/*N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) system using the following molar ratio: $[SSS]_0$:$[PVDF$-$CCl_3]_0$:$[CuCl]_0$:$[PMDETA]_0$ = 80:1:2:2 for a monomer concentration $[SSS]_0 = 1.5$ mol·L^{-1}. Aliquots were withdrawn periodically, and the monomer conversion was assessed by ^1H NMR, as previously described. Figure 8 exhibits the kinetic plots of the polymerization.

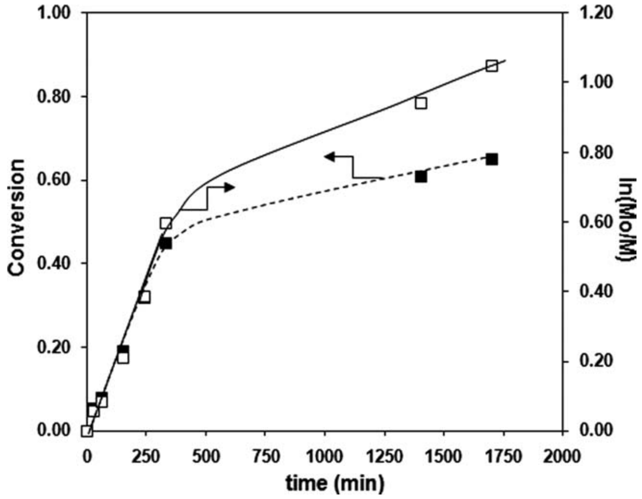


FIGURE 8 Kinetics plots of atom transfer radical polymerization (ATRP) of sodium styrene sulfonate (SSS) initiated by $PVDF_{46}$-CCl_3 and catalyzed by a CuCl/PMDETA complex in DMSO at 80 °C. Conditions: $[SSS]_0$:$[PVDF$-$CCl_3]_0$:$[CuCl]_0$:$[PMDETA]_0$ = 80:1:2:2 and $[SSS]_0 = 1.5$ mol L^{-1}.

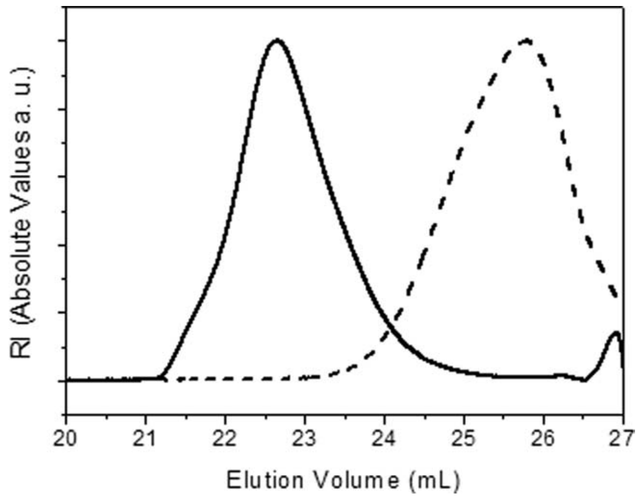


FIGURE 9 Size exclusion chromatography traces of PVDF$_{19}$-CCl$_3$ macroinitiator (dashed line) and PVDF$_{19}$-*b*-PSSS block copolymer (straight line) in NMP + 10^{-1} M LiBr.

The evolution of ln([M]$_0$/[M]) versus time is linear up to 50% of monomer conversion indicating the constant concentration of active species. Thereafter, the reaction slows down, which is marked by downward curvature. This can be attributed to the presence of termination reactions. A similar behavior was shown by Monge et al.[47] in the case of ATRP of methyl methacrylate, butyl methacrylate, and dimethylaminoethylmethacrylate in DMSO at 90 °C. We could not confirm the controlled behavior by checking the linear evolution of the molecular weights with conversion because the produced copolymers were not soluble in common SEC solvents as mentioned above for the ITP. However, SEC of the purified PVDF$_{19}$-*b*-PSS copolymer could be performed in NMP + 10^{-1} M LiBr (Fig. 9). This analysis confirmed the complete consumption of the macroinitiator and, thus, the quantitative efficiency of the initiation step. The block copolymer exhibited a number-average molar mass of 20,600 g mol^{-1} (PS standards) and a PDI of 1.9.

Proton NMR spectroscopy of the copolymer (Fig. 10) allowed us to assess DP$_n$ values of the PSSS block by comparison between the integrals of the protons of methylene groups in the PVDF block at 2.6–3.0 ppm with those of the aromatic ring of the PSSS block (ranging between 6.2 and 7.8 ppm). The DP$_n$ value of the PSSS block was 22, which is, within the experimental error, very close to the theoretical one of 23 (conversion of 70% for a [M]$_0$/[PVDF$_{19}$-CCl$_3$]$_0$ ratio of 35). Thus, it is possible to synthesize PVDF-*b*-PSSS diblock copolymers, in one step, from trichloromethyl-functionalized PVDF with a good control of the chain lengths.

ATRP of SSE from PVDF-CCl$_3$

It was of interest to compare the polymerization behaviors of SSS and SSEt in ATRP and ITP. Hence, ATRP of SSE was carried out, in DMF at 80 °C, in the presence of PVDF$_{70}$-CCl$_3$ as the macroinitiator and catalyzed by CuCl/PMDETA complex. The following molar ratio was used: [SSE]$_0$:[PVDF-CCl$_3$]$_0$:[CuCl]$_0$:[PMDETA]$_0$ = 90:1:2:2 for a monomer concentration [SSE]$_0$ = 1.5 mol·L^{-1}. Although the evolution of monomer conversion (monitored by GC) followed a first-order kinetics (Fig. 11), the DP$_n$ values (DP$_{SSE}$ = 112) assessed by ^{1}H NMR were higher than that of the theoretical one (DP$_{SSE(th)}$ = 76), indicating a poor control of the polymerization. Furthermore, ^{1}H NMR revealed the loss of the ethyl group during the polymerization process. It can be concluded that side reactions involving the ethyl sulfonate moieties occurred, leading to a noncontrolled polymerization of the monomer. SEC trace of a copolymer synthesized in the same fashion from a PVDF$_{46}$-CCl$_3$ (performed in NMP + 10^{-1} M LiBr) revealed a multimodal distribution of population (PDI = 6.0), indicating a poor control of the polymerization probably due to transfer reactions to the ethylsulfonate groups (Fig. 12).

EXPERIMENTAL

Materials

4-Styrenesulfonic acid sodium salt (SSS), bromoethane (>99%), perfluorohexyl iodide (99%), PMDETA (99%), copper chloride I (CuCl, 99.999%), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%), diphenyl ether (>99%), AgNO$_3$ solution (1 mol·L^{-1}), tetrabutylammonium hydroxide solution (55–60% in water), dioxane, and chloroform were purchased from Aldrich and used without further purification. Acetonitrile, DMSO, and DMF were purchased from Aldrich and distilled before use.

Synthesis of SSE

SSE was prepared following the procedure described previously.[48] During the whole synthesis, exposure to light should be avoided. SSS (40 g, 0.194 mol) was dissolved in water (200 mL). A 1 M AgNO$_3$ solution (216 mL, 0.216 mol) was added dropwise to the solution of SSS, at 0 °C. The mixture was stirred for 2 h. The white precipitate was filtered off and washed with water and diethyl ether. The solid, styrene sulfonate silver salt, was dissolved in acetonitrile, filtered,

FIGURE 10 ^{1}H NMR spectrum of PVDF$_{19}$-*b*-PSSS$_{22}$ diblock copolymer (recorded in DMSO-d_6).

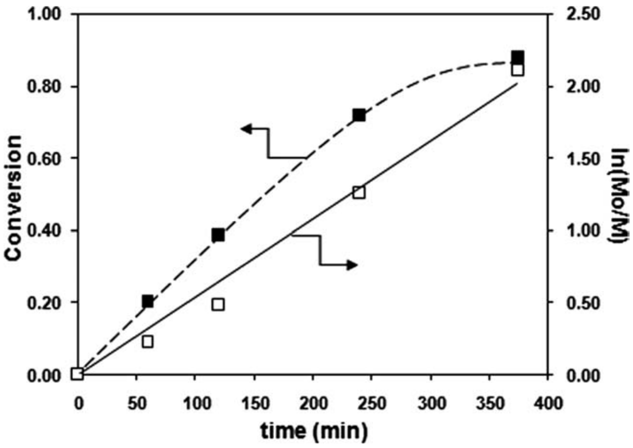


FIGURE 11 Kinetics plots of atom transfer radical polymerization (ATRP) of styrene sulfonate ethyl ester initiated by $PVDF_{70}$-CCl_3 and catalyzed by a CuCl/PMDETA complex in DMF at 80 °C. Conditions: $[SSE]_0$:$[PVDF\text{-}CCl_3]_0$:$[CuCl]_0$:$[PMDETA]_0$ = 90:1:2:2 and $[SSE]_0$ = 1.5 mol L^{-1}.

and evaporated under reduced pressure. The product was then coevaporated twice with 1,4-dioxane. The dry styrene sulfonate silver salt was dissolved in acetonitrile (250 mL) and 38.8 mL of ethyl bromide (0.66 mol) was added. The mixture was refluxed (70 °C) for 15 h. The mixture was filtered on Celite and evaporated under reduced pressure. A pale yellow liquid was obtained. Yields: 60–70%.

^{1}H NMR (DMSO-d_6) δ (ppm): 1.19 (t, 3H, $\mathbf{CH_3}$—CH_2—O—SO_2—), 4.09 (q, 2H, CH_3—$\mathbf{CH_2}$—O—SO_2—), 5.50 and 6.06 (2 doublets, 2 × 1H, $\mathbf{CH_2}$=CH—C_6H_5), 6.86 (dd, 1H, CH_2=C$\mathbf{H}$—C_6H_5), 7.75 and 7.86 (2 doublets, 2 × 2H, aromatic protons).

Radical Polymerizations

Synthesis of PVDF-I

PVDF bearing iodide chain ends was synthesized by ITP of VDF with $C_6F_{13}I$ according to the procedure described by Boyer et al.[49]

Synthesis of PVDF-CCl_3

PVDF bearing trichloromethyl end groups was synthesized according to the procedure described by Duc et al.[46]

Typical Procedure of ITP of SSS

SSS, CTA (either $C_6F_{13}I$ or PVDF-I), and AIBN were placed in a Schlenk flask and dissolved in the appropriate solvent (DMF/water (80/20) mixtures for ITP in the presence of $C_6F_{13}I$ or DMSO for ITP in the presence of PVDF-I). The reaction mixture was degassed by three freeze-pump-thaw cycles and backfilled with argon. The mixture was stirred at 70 °C. Aliquots were periodically sampled to assess the monomer conversion by ^{1}H NMR spectroscopy.

Typical Procedure of ITP of SSE

SSE, CTA (either $C_6F_{13}I$ or PVDF-I), and AIBN were placed in a Schlenk flask and dissolved in the appropriate solvent (acetonitrile for ITP in the presence of $C_6F_{13}I$ or DMF for ITP in the presence of PVDF-I). Diphenyl ether was added as an internal standard to monitor the monomer conversion by GC. The reaction mixture was degassed by three freeze-pump-thaw cycles and backfilled with argon. The mixture was stirred at 70 or 90 °C. Aliquots were periodically withdrawn to assess SSE conversion by GC.

Typical Procedure of ATRP of SSS Initiated by PVDF-CCl_3

CuCl in a Schlenk flask was degassed for 15 min by flowing argon. SSS, PVDF-CCl_3, and PMDETA were placed in a Schlenk flask and dissolved in DMSO. This mixture was degassed by three freeze-pump-thaw cycles, backfilled with argon, and transferred to the Schlenk flask containing CuCl via a canula. The mixture was stirred at 70 °C. Aliquots were periodically withdrawn to determine the conversion by ^{1}H NMR.

Typical Procedure of ATRP of SSE Initiated by PVDF-CCl_3

CuCl in a Schlenk flask was degassed for 15 min by flowing argon. SSE, PVDF-CCl_3, PMDETA, and diphenyl ether were placed in a Schlenk flask and dissolved in DMF. This mixture was degassed by three freeze-pump-thaw cycles, backfilled with argon, and transferred to the Schlenk flask containing CuCl via a canula. The mixture was stirred at 80 °C. Aliquots were periodically withdrawn to determine the conversion by GC.

Characterization

Gas Chromatography

Samples diluted in acetonitrile or DMF (depending of the polymerization solvent) were injected at a temperature of 250 °C on a GC-2014 system from Shimadzu equipped with an AOC-20i autoinjector. An Equity-1 capillary column (length: 30 m, 0.25-mm internal diameter, film thickness 0.25 mm) was used as the stationary phase and nitrogen as the mobile phase. Separation for the determination of monomer conversion was performed using the following temperature program: 1 min at 60 °C, heating at 60 °C/min from 60 to 150 °C, and maintaining at 150 °C for 18 min. The components

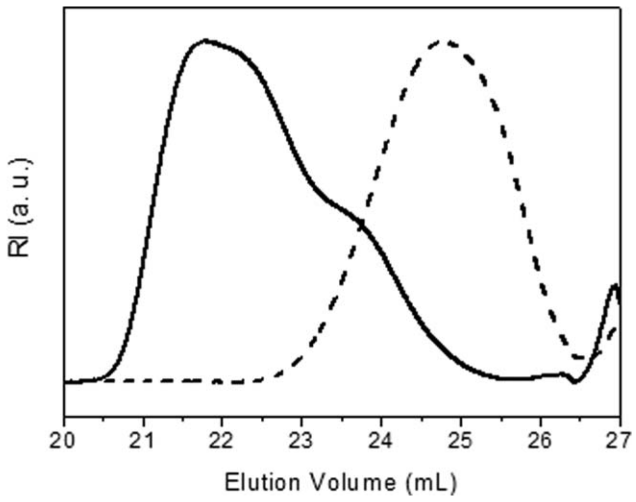


FIGURE 12 Size exclusion chromatography traces of $PVDF_{46}$-CCl_3 macroinitiator (dashed line) and $PVDF_{46}$-*b*-PSSE block copolymer (full line) in NMP + 10^{-1} M LiBr.

were detected with a flame ionization detector operating at 250 °C. Monomer conversion was determined using the peaks area ratio of monomer and diphenyl ether.

Size Exclusion Chromatography

SEC was carried out in water at 20 °C, at a flow rate of 1 mL min^{-1} using a TSK PW 500 column of 30 cm and a TSK PW 600 column of 60 cm in series and a refractive index detector. The elution solvent was 0.1 M $NaNO_3$ at pH 7. Mass distributions were obtained in terms of the molar mass equivalent to pullulan standards.

SEC was carried out in NMP (containing 10^{-1} M LiBr) at 60 °C, at a flow rate of 0.5 mL min^{-1}, by means of a Viscotek TDA 302 apparatus and a set of three columns PL Gel (Polymer Laboratories) 10 m connected in series. Monodispersed (PS) standards were used for calibration. The dried polymers were first dissolved in water. NMP (containing 10^{-1} M LiBr) was added and water was removed by evaporation before injection in the SEC apparatus.

NMR Spectroscopy

NMR spectra were recorded on a Bruker AC-400 spectrometer for ^1H NMR (400 MHz) and $CDCl_3$ or DMSO-d_6 as the solvents. Chemical shifts are reported in ppm relative to the reference (TMS) resonance.

CONCLUSIONS

The preparation of PVDF-*b*-PSSS block copolymer was possible through two polymerizations techniques: ITP and ATRP and via a direct polymerization of SSS monomer. ITP of SSE, a protected monomer, in the presence of PVDF-I macromolecular CTA led to rather well-defined copolymers chains in spite of side reactions with the ethyl sulfonate groups. This work showed that, for the ITP of styrene sulfonate derivatives, the PVDF-I macromolecular CTA is not totally efficient because a limitation of the CTA consumption was observed. This can be explained by both a low activity of the CTA and a fast propagation rate of the monomer. Thus, it was possible to obtain PVDF-based block copolymers by this technique, but the copolymers are mixed with unreacted PVDF-I. The use of ATRP overcomes from this drawback. Although ATRP of SSE seemed not to be suitable to obtain block copolymers, it was shown that the direct ATRP of SSS exhibited a controlled behavior in a certain range of conversion giving the opportunity to lead to PVDF-*b*-PSSS block copolymers with a rather good control of the chain length and acceptable polydispersity indices.

The authors thank the Agence Nationale pour la Recherche (ANR) for funding the MENHYR project part of the PANH program. Alain Rameau (ICS, Strasbourg, France) is acknowledged for the SEC analyses in NMP.

REFERENCES AND NOTES

1 Prakash, G. K. S.; Smart, M. C.; Wang, Q. J.; Atti, A.; Pleynet, V.; Yang, B.; McGrath, K.; Olah, G. A.; Narayanan, S. R.; Chun, W.; Valdez, T.; Surampudi, S. J Fluor Chem 2004, 125, 1217–1230.

2 Zapata, P.; Mountz, D.; Meredith, J. C. Macromolecules 2010, 43, 7625–7636.

3 Moszczynski, P.; Kalita, M.; Parzuchowski, P.; Siekierski, M.; Wieczorek, W. J Power Sources 2007, 173, 648–656.

4 Piboonsatsanasakul, P.; Wootthikanokkhan, J.; Thanawan, S. J Appl Polym Sci 2008, 107, 1325–1336.

5 Hamley, I. W. The Physics of Block Copolymers; Oxford University Press: Oxford, 1998.

6 Hadjichristidis, N.; Pitsikalis, M.; Iatrou, H. Adv Polym Sci 2005, 189, 1–124.

7 Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. Macromolecules 1996, 29, 5590–5598.

8 Braunecker, W. A.; Matyjaszewski, K. Prog Polym Sci 2007, 32, 93–146.

9 Ameduri, B. Macromolecules 2010, 43, 10163–10184.

10 Valade, D.; Boyer, C.; Ameduri, B.; Boutevin, B. Macromolecules 2006, 39, 8639–8651.

11 Destarac, M.; Matyjaszewski, K.; Silverman, E.; Ameduri, B.; Boutevin, B. Macromolecules 2000, 33, 4613–4615.

12 Jo, S. M.; Lee, W. S.; Ahn, B. S.; Park, K. Y.; Kim, K. A.; Paeng, I. S. R. Polym Bull 2000, 44, 1–8.

13 Shi, Z. Q.; Holdcroft, S. Macromolecules 2004, 37, 2084–2089.

14 Xu, K.; Li, K.; Khanchaitit, P.; Wang, Q. Chem Mater 2007, 19, 5937–5945.

15 Kostov, G.; Boschet, F.; Buller, J.; Badache, L.; Brandsadter, S.; Ameduri, B. Macromolecules 2011, 44, 1841–1855.

16 Elabd, Y. A.; Hickner, M. A. Macromolecules 2011, 44, 1–11.

17 Shi, Z. Q.; Holdcroft, S. Macromolecules 2005, 38, 4193–4201.

18 Rubatat, L.; Shi, Z. Q.; Diat, O.; Holdcroft, S.; Frisken, B. J. Macromolecules 2006, 39, 720–730.

19 Boyer, C.; Valade, D.; Lacroix-Desmazes, P.; Ameduri, B.; Boutevin, B. J Polym Sci Part A: Polym Chem 2006, 44, 5763–5777.

20 Tatemoto, M.; Nakagawa, T. (Daikin Kogyo Co. Ltd., Japan). German Offen DE2729671, 30-06-1976 (Chem. Abst. 88 (1978) 137374).

21 Gabaston, L. I.; Furlong, S. A.; Jackson, R. A.; Armes, S. P. Polymer 1999, 40, 4505–4514.

22 Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559–5562.

23 Iddon, P. D.; Robinson, K. L.; Armes, S. P. Polymer 2004, 45, 759–768.

24 Choi, C. K.; Kim, Y. B. Polym Bull 2003, 49, 433–439.

25 Oikonomou, E. K.; Pefkianakis, E. K.; Bokias, G.; Kallitsis, J. K. Eur Polym J 2008, 44, 1857–1864.

26 Li, C. M.; Yang, J.; Wang, P. Y.; Liu, J.; Yang, Q. H. Microporous Mesoporous Mater 2009, 123, 228–233.

27 Zhai, G. Q.; Kang, E. T.; Neoh, K. G. Macromolecules 2004, 37, 7240–7249.

28 Chen, X. Y.; Randall, D. P.; Perruchot, C.; Watts, J. F.; Patten, T. E.; von Werne, T.; Armes, S. P. J. Coll Int Sci 2003, 257, 56–64.

29 Kong, H.; Luo, P.; Gao, C.; Yan, D. Polymer 2005, 46, 2472–2485.

30 Li, L.; Yan, G. P.; Wu, J. Y.; Yu, X. H.; Guo, Q. Z. e-Polymers 2009, 10.

31 Niepceron, F.; Lafitte, B.; Galiano, H.; Bigarre, J.; Nicol, E.; Tassin, J. F. J Membr Sci 2009, 338, 100–110.

32 Xu, F. J.; Xu, D.; Kang, E. T.; Neoh, K. G. J Mater Chem 2004, 14, 2674–2682.

33 Ameduri, B.; Boutevin, B. Well-Architectured Fluoropolymers: Synthesis, Properties and Applications; Elsevier: Amsterdam, 2004.

34 Ameduri, B. Chem Rev 2009, 109, 6632–6686.

35 David, G.; Boyer, C.; Tayouo, R.; Seabrook, S.; Ameduri, B.; Boutevin, B.; Woodward, G.; Destarac, M. Macromol Chem Phys 2008, 209, 75–83.

36 Durand, N.; Ameduri, B.; Takashima, K.; Ishida, K.; Horie, S.; Ueda, Y. Polymer J (Japan) 2011, 43, 171–179.

37 Baigl, D.; Seery, T. A. P.; Williams, C. E. Macromolecules 2002, 35, 2318–2326.

38 Kucera, F.; Jancar, J. Polym Eng Sci 1998, 38, 783–792.

39 Lienkamp, K.; Ruthard, C.; Lieser, G.; Berger, R.; Groehn, F.; Wegner, G. Macromol Chem Phys 2006, 207, 2050–2065.

40 Lienkamp, K.; Schnell, I.; Groehn, F.; Wegner, G. Macromol Chem Phys 2006, 207, 2066–2073.

41 Okamura, H.; Takatori, Y.; Tsunooka, M.; Shirai, M. Polymer 2002, 43, 3155–3162.

42 Tillet, G.; Boutevin, B.; Ameduri, B. Prog Polym Sci 2011, 36, 191–217.

43 David, G.; Boyer, C.; Tonnar, J.; Ameduri, B.; Lacroix-Desmazes, P.; Boutevin, B. Chem Rev 2006, 106, 3936–3962.

44 Boutevin, B.; Pietrasanta, Y.; Bauduin, G. Makromol Chem 1985, 186, 283–295.

45 Duc, M.; Ameduri, B.; Boutevin, B.; Kharroubi, M.; Sage, J.-M. Macromol Chem Phys 1998, 199, 1271–1289.

46 Duc, M.; Ameduri, B.; David, G.; Boutevin, B. J Fluor Chem 2007, 128, 144–149.

47 Monge, S.; Darcos, V.; Haddleton, D. M. J Polym Sci Part A: Polym Chem 2004, 42, 6299–6308.

48 Sikkema, F. D.; Comellas-Aragones, M.; Fokkink, R. G.; Verduin, B. J. M.; Cornelissen, J.; Nolte, R. J. M. Org Biomol Chem 2007, 5, 54–57.

49 Boyer, C.; Valade, D.; Sauguet, L.; Ameduri, B.; Boutevin, B. Macromolecules 2005, 38, 10353–10362.