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Synthesis and ATRP of novel fluorinated aromatic monomer with pendant sulfonate group

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ABSTRACT

Novel, fluorinated monomer with pendant sulfonate group was synthesized utilizing a two-step derivatization of 2,3,4,5,6-pentafluorostyrene (FS). The first step was a nucleophilic substitution of the fluorine atom in *para* position by hydroxyl group followed by sulfopropylation. The monomer was polymerized under aqueous ATRP conditions to yield phenyl-fluorinated aromatic homopolymer bearing pendant sulfonates on each repeating unit. Furthermore, this polymer was used as macroinitiator for the ATRP of poly(ethylene glycol) methacrylate. The polymers were characterized by ^{1}H NMR, SEC and FTIR analyses. Their thermal properties were evaluated by differential scanning calorimetry and thermal gravimetric analyses.

1. Introduction

Polymers with high content of sulfonic acid groups represent a class of water-soluble polymers and anionic polyelectrolytes [1]. They have attracted much interest in numerous bio-related applications based on specific acid–base and oppositely charged ionic interactions with biologically active molecules [2–4]. Sulfonic acid-based polymer materials have been developed as blood-compatible coatings [5], cationic drug-delivery systems [6], and enzyme carriers [7]. Sulfonic acid-containing amphiphilic block copolymers, on the other hand, are of considerable and increasing interest, mainly due to their ability to form highly ordered structures as a result of self-association and their potential applications as proton conductive membranes [8–10]. The synthesis of well-defined polymers with sulfonic acid groups applying various controlled radical polymerization (CRP) methods has been described in the literature [11–13]. Sulfonic acid-containing block copolymers were also prepared by controlled radical polymerization of monomer derivatives with protected sulfonic acid groups [14,15] or by post-modification [16].

Fluorinated polymers have attracted significant attention due to a series of favorable properties, such as high thermal stability, hydrophobicity, good chemical resistance, low flammability as well as their optical and electrical properties [17,18]. Most fluorinated monomers can be polymerized under radical conditions, and the processes that enable CRP of hydrocarbon monomers can be easily adapted for that of fluoromonomers [19]. Thus, 2,3,4,5,6-pentafluorostyrene (FS) has been polymerized in controlled manner by atom transfer radical polymerization (ATRP) yielding fully phenyl fluorinated polystyrene (PFS) [20]. The potential of ATRP has been further exploited for the synthesis of PFS-based linear di-, multiblock- or star-shaped architectures [20–22]. Furthermore, various 4-substituted-2,3,4,5-tetrafluorostyrene derivatives were synthesized and successfully polymerized by ATRP [23,24]. Other CRP methods for the preparation of 4-substituted FS-based copolymers include nitroxide-mediated polymerization (NMP) or reversible addition-fragmentation chain transfer (RAFT) followed by post-modifications [25,26].

Herein, we present the synthesis and controlled polymerization of novel fluorinated aromatic monomer bearing pendant sulfonate group. A synthetic strategy based on nucleophilic substitution of the fluorine atom in *para* position of FS followed by sulfopropylation is utilized for the monomer preparation. The controlled polymerization of the newly synthesized monomer under aqueous ATRP conditions is demonstrated as well as attempts for block-copolymer synthesis. Furthermore, the thermal properties of the sulfonated homopolymer are compared to those of PFS.

2. Results and discussion

2.1. Synthesis of tetrafluorostyrene alkyl sulfonated monomer (TFSSNa)

The synthetic procedure is shown on Scheme 1. It involves modification of FS exploiting the well known fact in organic synthesis that the labile *para*-fluorine of the pentafluorophenyl

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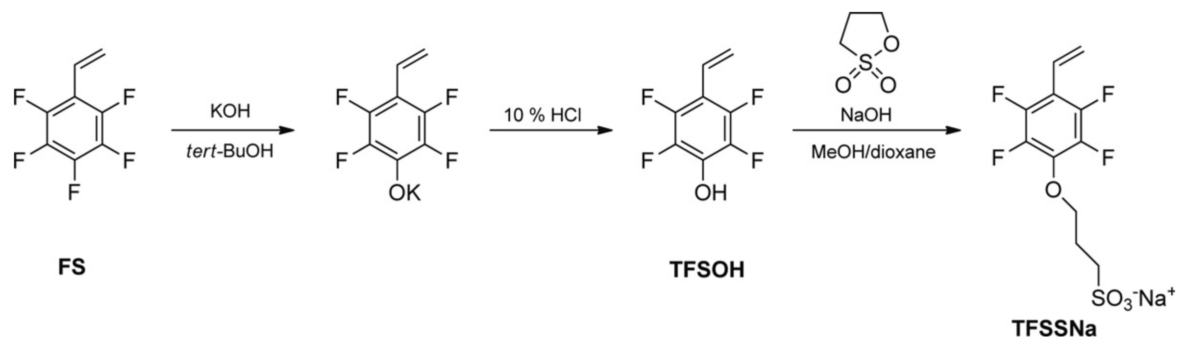


Scheme 1. Synthesis of fluorinated monomer with pendant sulfonate group TFSSNa.

groups can undergo a nucleophilic substitution. Initially, FS was converted into a *para*-hydroxy-tetrafluorostyrene derivative (TFSOH). Usually this is done in two steps – nucleophilic substitution of FS by sodium methoxide followed by demethylation with boron tribromide as described by Pitois et al. [27]. A drawback of this procedure is the difficult separation of *para*-hydroxy substituted tetrafluorostyrene from the unreacted methoxy derivative due to their close boiling temperatures. In our case we used the more recently reported two step procedure to obtain para-hydroxy derivative of FS [28]. TFSOH was obtained in one pot reaction of FS with alkaline *tert*-BuOH followed by acidification (Scheme 1). After careful extractions and vacuum distillation the hydroxy derivative was obtained with 95% purity and 60% yield. The final step in the monomer preparation was the attachment of pendant sulfonate groups in *para*-position of the aromatic ring through a sulfopropylation. We have previously shown that fluorinated and non-fluorinated aromatic copolymers can be successfully sulfopropylated by a nucleophilic ring-opening reaction of 1,3-propane sultone (PrS) [16,29]. In the current work we applied this approach to obtain a sulfopropylated tetrafluoro derivative of styrene. The hydroxy group of TFSOH was activated in alkaline MeOH and used for the ring-opening of PrS. Regardless of the availability of four highly hydrophobic fluorine atoms and a propylate group attached to the aromatic ring, the presence of a single pendant sulfonate group renders the monomer completely soluble in water. The overall yield of the monomer was 41%. The successful and complete sulfopropylation was confirmed by ^{1}H NMR in D_2O (Fig. 1). The resonances at 4.42, 3.14, and 2.22 ppm corresponding to one oxymethylene and two methylene protons from the attached sulfopropylate side groups appeared in the product's spectrum and their relative intensities compared to those of the vinyl protons at 6.68, 6.08 and 5.72 suggested complete functionalization and high purity of the monomer obtained. The successful sulfopropylation was further confirmed by FTIR spectroscopy. Characteristic absorption bands for the asymmetric and symmetric O=S=O stretch of the sulfonate groups were found at 1183 and 1060 cm^{-1}, respectively in the monomer's spectrum.

2.2. ATRP of TFSSNa

Generally, the controlled polymerization of monomers containing strong acidic groups under ATRP conditions is hampered due to the sensitivity of the polymerization-control complex to acidic media. Recently, Iddon et al. [13] reported an aqueous ATRP of sodium 4-styrenesulfonate (NaSS) at 20 °C. The water was needed to dissolve the ionic monomer, while different amounts of methanol were added to slow down the polymerization rate and to achieve better control over the process. Due to the aromatic nature of $TFSSO_3Na$ we decided to use similar conditions for the ATRP of the newly synthesized sulfonated monomer. The ATRP of TFSSNa was performed in water/methanol = 3:1 (v/v) solvent mixture at 25 °C and was initiated by 4-(bromomethyl)benzoic acid (BMBA) in sodium salt form (Scheme 2). After 24 h of polymerization, followed by dialysis and lyophilization, the purified product was recovered as white powder in 85% yield.

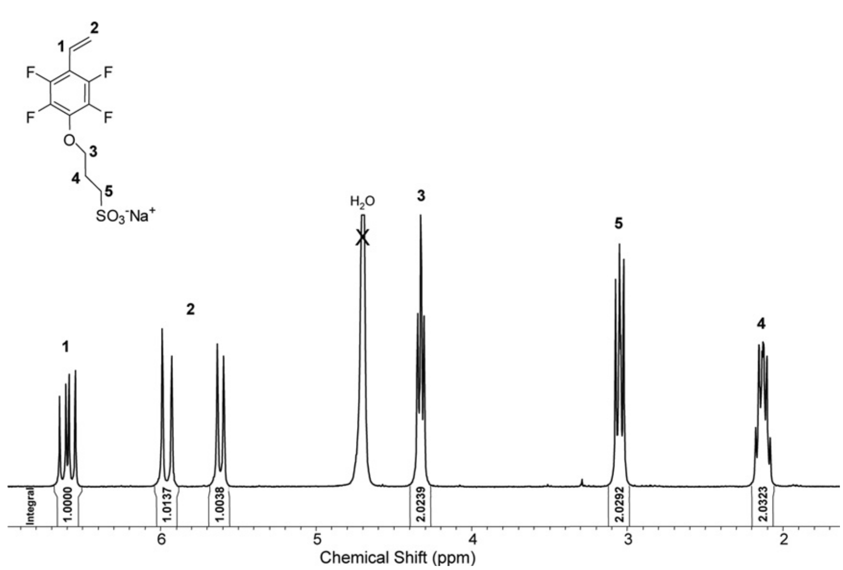
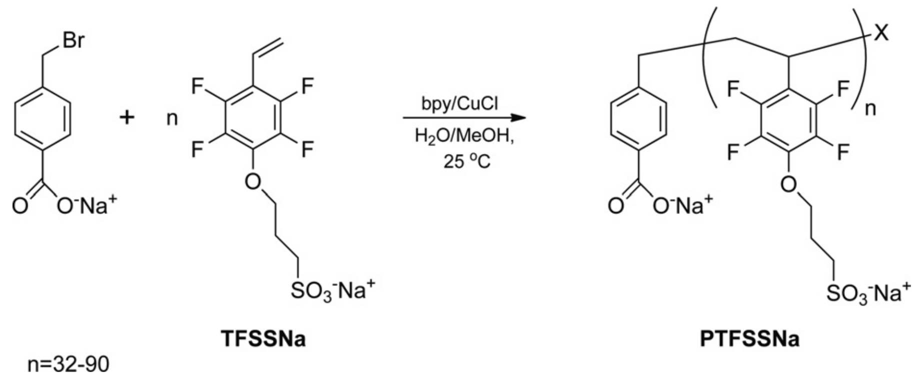


Fig. 1. ^{1}H NMR (300 MHz) spectrum of TFSSNa in D_2O at 25 °C.



Scheme 2. ATRP of TFSSNa.

The [1]H NMR spectrum of PTFSSNa is presented in Fig. 2a. It clearly shows the peaks at 2.1 and 3.1 ppm attributed to the two methylene protons from the pendant sulfopropylate groups and the overlapping backbone protons as well as the peak at 4.3 ppm attributed solely to the oxymethylene protons next to the aromatic ring. The molar mass and polydispersity index (PDI) of the polymer were estimated by aqueous SEC. A typical SEC trace of the sulfonated polymer is shown in Fig. 2b. It reveals that the polymers elute as monomodal species with polydispersity indices in 1.3–1.35 range. The molar masses were estimated *versus* PNaSS narrow molar mass standards and were found to be in a good agreement with the targeted ones. Homopolymers with molar masses ranging from approx. 10,000 to 30,000 were synthesized.

For the kinetic studies the polymerization was performed in a mixture of deuterated water and methanol under the same ATRP conditions over a period of 180 min. At predetermined time intervals samples were withdrawn and subjected to NMR analyses. The degree of monomer conversion was estimated from the relative intensities of the protons at 6.6, 6.0 and 5.7 ppm attributed to the monomer's olefinic protons and the oxymethylene protons from the pendant sulfopropylate groups at 4.3 ppm. The corresponding semilogarithmic plot of monomer conversion *versus* time reveals a slight curvature as shown in Fig. 3. This suggests a deviation from the ideal living character of the process, most likely due to the non-constant polymer radical concentration during the polymerization [13,30]. However, the deviation from the linearity

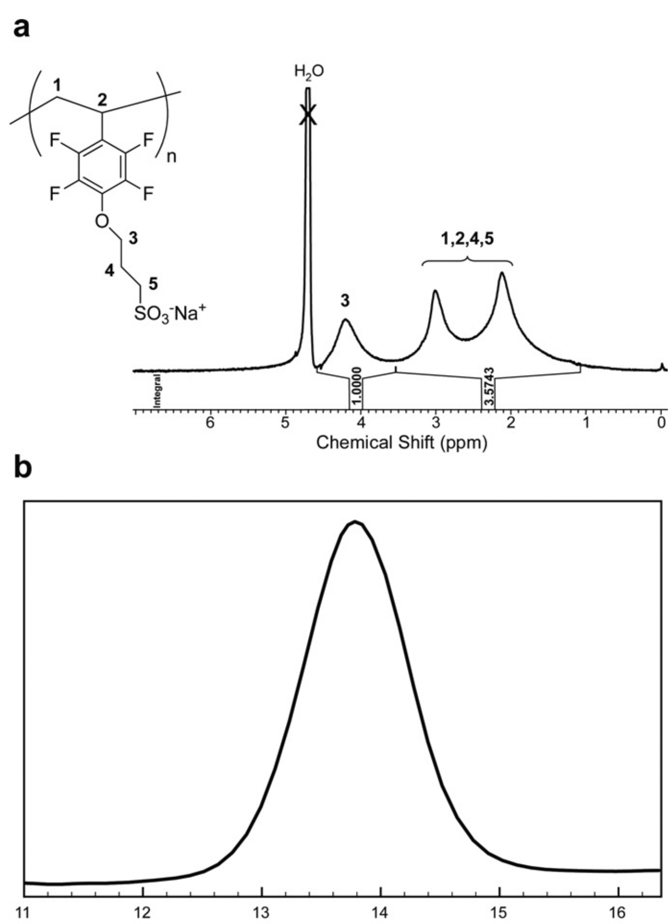


Fig. 2. [1]H NMR (300 MHz) spectrum of PTFSSNa in D_2O at 25 °C (a) and size exclusion chromatogram of PTFSSNa (M_n = 10 700 Da, M_w/M_n = 1.35) (b).

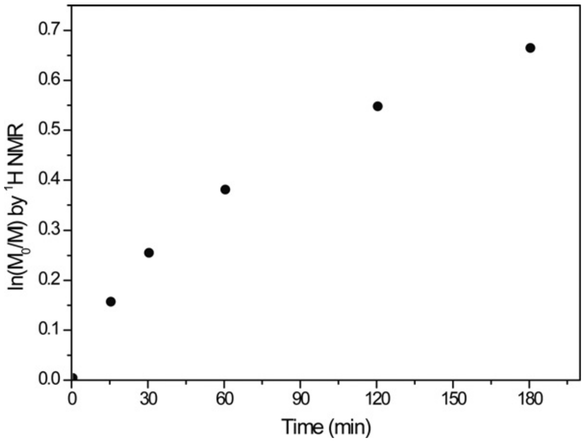


Fig. 3. Semi-logarithmic kinetic plots for the homopolymerization of TFSSNa at 25 °C using the BMBA initiator and CuCl catalyst in 3:1 water/methanol mixture.

is much less pronounced and the polymerization rate is much slower as compared to the ATRP of NaSS performed under similar conditions by Iddon et al. [13].

2.3. Block copolymerization. Synthesis of PTFSSNa-b-PPEGMA

The synthesized polyionic fluorinated aromatic homopolymers (PTFSSNa) were used as macroinitiators to test the possibility of obtaining diblock copolymers. A poly(ethylene glycol) methacrylate (PEGMA) with molar mass of approx. 360 Da was chosen as a building segment for the second block due to its good solubility in the water/methanol solvent mixture and the distinct resonances in ^{1}H NMR. The ATRP was performed at 30 °C using the same solvent mixture and CuCl/bpy catalytic system. The targeted degree of polymerization (DP) was 60 in order to obtain a clear shift in the SEC trace of block copolymer. The product was dialyzed to remove the unreacted PEGMA-monomer and subjected to ^{1}H NMR and SEC analyses. The ^{1}H NMR spectrum of the product in D_2O confirms the presence of oxyethylene protons from the PEGMA-side groups (Fig. 4a). The SEC analysis shows a distinct shift toward lower elution volume (higher molar mass) for the block copolymer (Fig. 4b). However, there is also a leftover of the macroinitiator in the block copolymer's SEC-trace indicating an incomplete initiating efficiency of *PTFSSNa*. This is most likely due to the incomplete halogen chain-end functionalization since the macroinitiator used for the block copolymer synthesis was obtained at 100% monomer conversion.

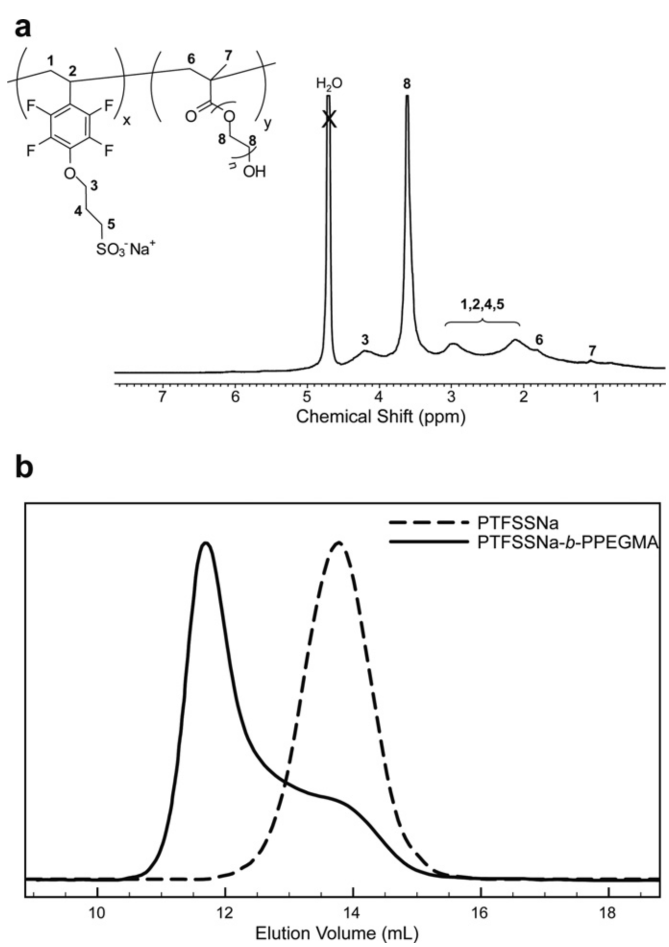


Fig. 4. ^{1}H NMR (300 MHz) spectrum in D_2O at 25 °C of PTFSSNa-b-PPEGMA (a) and SEC overlay of PTFSSNa-macroinitiator and PTFSSNa-b-PPEGMA (b).

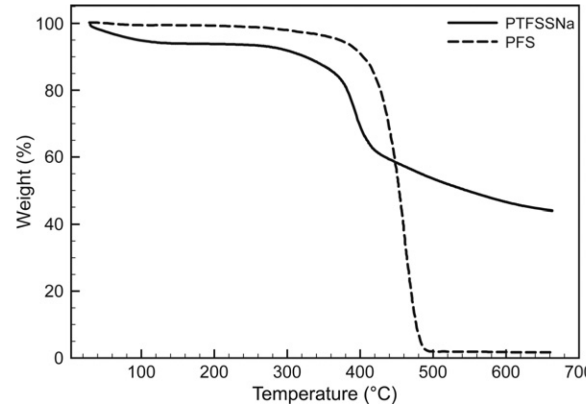


Fig. 5. TGA curves for PFS (a) and PTFSSNa (b).

2.4. Thermal properties of PTFSSNa

The thermal properties of the newly synthesized fluorinated homopolymers with pendant sulfonate groups were evaluated by their thermal decomposition (T_d) and glass transition (T_g) data measured by TGA and DSC respectively. The sulfonated polymers exhibit lower thermal stability compared to the fully phenyl-fluorinated polystyrene (PFS) which is thermally stable up to 390 °C (Fig. 5). The sulfonated polymers start to decompose at 330 °C after an initial loss of water. Moreover, two-step degradation is observed for *PTFSSNa*. The first step is attributed to the degradation of the pendant sulfopropylate groups. The main weight loss starts above 380 °C, close to the decomposition temperature of PFS, and is connected with the degradation of the backbone chain.

The sulfonated aromatic fluoropolymers showed higher glass-transition temperatures compared to those of PFS. The sulfonated polymer PTFSSNa with molar mass of 10 700 has a T_g of 134 °C, whereas the T_g of PFS of comparable molar mass is 94 °C [20]. A similar increase in the T_g was previously observed by us after the attachment of pendant sulfonate groups onto a polymer backbone. The increase was attributed to hydrogen bonding in the sulfonated polymers which prevails over the plasticizing effect of the short side alkyl chains [29].

3. Conclusion

A novel aromatic fluorinated monomer with pendant alkyl-sulfonate group was synthesized and polymerized under aqueous ATRP conditions. The monomer was prepared in two reaction steps from 2,3,4,5,6-pentafluorostyrene through a nucleophilic substitution of the labile *para*-fluorine atom by hydroxyl group followed by sulfopropylation with 1,3-propanesultone. The monomer was polymerized in controlled manner *via* ATRP in water/methanol to yield well-defined fluorinated aromatic homopolymers bearing pendant sulfonate groups on each repeating unit. The polymers were characterized by ^{1}H NMR and SEC analyses. Their thermal properties were investigated by TGA and DSC. A diblock copolymer was also obtained using the newly synthesized polymer as ATRP-macroinitiator. The synthesized fluorinated polymers with sulfonate side groups might be used as building blocks for numerous bio-related applications as well as for polymer electrolytes in fuel cells.

4. Experimental

4.1. Materials

The chemicals were purchased from Sigma–Aldrich. 2,3,4,5,6-Pentafluorostyrene (FS, 99%) was passed through an inhibitor-removing column and distilled under reduced pressure prior to use. Poly(ethylene glycol) methacrylate (PEGMA, $M_n \sim 360$ Da) was passed through a column containing neutral aluminum oxide. Methanol (MeOH, >99%), 1,4-dioxane (DO, >99%), and dichloromethane (DCM, >99.8%) were dried using standard procedures. 1,3-Propane sultone (PrS, 98%), 4-(bromomethyl)benzoic acid (BMBA, 97%), copper(I) chloride (CuCl, 98%), potassium hydroxide (KOH, >85%), sodium hydroxide (NaOH, >98%), tertiary butanol (*tert*-BuOH, >99.5%), diethyl ether (>99.8%), and 2,2′-bipyridyl (bpy, 99%) were used as received.

4.2. Instrumentation

^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument. Size exclusion chromatography (SEC) was performed in MeOH/H_2O = 1:1 (v/v) mixture + 50 mM NaCl at a flow rate of 1.0 mL min^{-1} on a set of PW4000 + PW2500 columns (Tosoh Corp., Tokyo, Japan), calibrated *versus* poly(sodium styrene sulfonate) narrow molar mass standards; the column temperature was 25 °C and DRI detector temperature was 37 °C. Infrared spectra were recorded on a PerkinElmer Spectrum One model 2000 Fourier transform infrared system with a universal attenuated total reflection sampling accessory on a ZnSe/diamond composite. Thermal analyses were carried out on a differential scanning calorimeter DSC Q1000 (TA Instruments) in a temperature range of 20–250 °C at a heating and cooling rate of 10 °C min^{-1} under nitrogen. The glass transition temperatures (T_g) were determined during the second heating cycle at the inflection point of the thermal transition. Thermogravimetric analyses (TGA) were performed on a TGA Q500 instrument measuring the samples' total weight loss from 25 to 650 °C at a rate of 10 °C min^{-1} under a nitrogen flow of 90 mL min^{-1}.

4.3. Synthesis of 2,3,5,6-tetrafluoro-4-vinylphenol (TFSOH)

The synthesis of TFSOH was performed similar to a previously reported procedure [28]. Briefly, FS (20 g, 0.1 mol) was added to a mixture of KOH (30 g, 0.53 mol) in 400 mL of *tert*-BuOH. The mixture was refluxed for 2 h, cooled down to room temperature and diluted with 1200 mL of water. The alcohol was distilled off and the residue was extracted with diethyl ether (3× 300 mL). The aqueous phase was acidified (pH ∼ 3) with 10 wt.% HCl and was extracted with diethyl ether (3× 300 mL). The organic phase was dried over $MgSO_4$ overnight. The solution was filtered and the diethyl ether was distilled off. The product was purified through a vacuum distillation. Yield: 11.5 g (58%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 11.62 (O*H*), 6.59 (C*H*═CH_2), 5.60–5.92 (CH═CH_2). FTIR (cm^{-1}): 3400 (OH).

4.4. Synthesis of sodium 3-(2,3,5,6-tetrafluoro-4-vinylphenoxy)propane-1-sulfonate (TFSSNa)

The hydroxy-functionalized monomer TFSOH (10 g, 0.052 mol) was dissolved in MeOH (315 mL) followed by the addition of NaOH (2.28 g, 0.057 mol). The mixture was stirred at room temperature until the base was completely dissolved. Finally, a solution of PrS (6.96 g, 0.057 mol) in 1,4-dioxane (26 mL) was added dropwise and the reaction mixture was stirred for an hour at room temperature. Then it was refluxed for 24 h. The solvents were evaporated and the residue was washed with DCM. The product was recrystallized twice from MeOH/H_2O = 2:1 (v/v). Yield: 12.2 g (70%). ^{1}H NMR (300 MHz, D_2O, δ, ppm): 6.68 (C*H*═CH_2), 6.08–5.68 (CH═CH_2), 4.42 (O–CH_2), 3.14 (CH_2–SO_3Na), 2.22 (CH_2–CH_2–CH_2). FTIR (cm^{-1}): 1183 and 1060 (O═S═O).

4.5. ATRP of TFSSNa – synthesis of homopolymers PTFSSNa

Typically, TFSSNa (1 g, 2.97 mmol) and the initiator BMBA (21.3 mg, 0.099 mmol) were dissolved in water (4.95 mL). A few drops of 1 M NaOH were added to the solution in order to adjust the pH ∼ 9–10. The alkaline mixture was degassed trice. Separately, CuCl (9.8 mg, 0.099 mmol) and bpy (30.9 mg, 0.198 mmol) were dissolved in 1.65 ml of MeOH and the complex solution was degassed trice. The two solutions were combined *via* a transfer needle and the reaction mixture was degassed one more time. The polymerization was performed at 25 °C for 24 h. The reaction mixture was dialyzed against distilled water for 4 days (M_w cut-off = 1200 Da) and the product was recovered through lyophilization. Yield: 0.85 g (85%). ^{1}H NMR (300 MHz, D_2O, δ, ppm): 4.27 (O–CH_2), 3.70–2.65 (C*H*–CH_2 + CH_2–SO_3Na), 2.63–1.1 (CH_2–CH_2–CH_2 + CH–CH_2). FTIR (cm^{-1}): 1185 and 1045 (O═S═O). Aqueous SEC (MeOH/H_2O = 1:1, v/v): M_n = 10,700 Da, M_w/M_n = 1.35.

The kinetic study was performed in D_2O/CD_3OD = 3:1 (v/v) solvent mixture and monomer to initiator ([M]:[I]) ratio = 90 applying the same ATRP conditions. At time intervals, an appropriate volume of the mixture was withdrawn with a degassed syringe and subjected to ^{1}H NMR analysis.

4.6. Synthesis of block copolymer PTFSSNa-b-PPEGMA

The macroinitiator *PTFSSNa* (0.2 g, 0.019 mmol) and PEGMA (0.41 g, 1.14 mmol) were dissolved in 2 mL of H_2O/MeOH = 3:1 (v/v) mixture and were degassed trice. Separately, CuCl (18.8 mg, 0.19 mmol) and bpy (59.35 mg, 0.38 mmol) were dissolved in 6.5 mL of H_2O/MeOH = 3:1 (v/v) mixture, degassed trice, and 0.65 mL were withdrawn *via* syringe and added to the monomer and macroinitiator solution. The combined brown-colored solution was degassed one more time and the polymerization was started at 30 °C. It was stopped after 3 h by passing air through the reaction mixture. The green solution was dialyzed against distilled water and the product was recovered through lyophilization. Yield: 0.42 g (67%). ^{1}H NMR (300 MHz, D_2O, δ, ppm): 4.60–4.00 (O═C–O–CH_2), 3.95–3.4 (O–CH_2–CH_2–O), 3.30–2.65 (Ar–C*H*–CH_2 + CH_2–SO_3Na), 2.63–1.1 (CH_2–CH_2–CH_2 + Ar–CH–CH_2 + C–CH_2), 1.05–0.6 (C–CH_3). FTIR (cm^{-1}): 1185 and 1043 (O═S═O), 1725 (C═O), 3440 (OH).

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