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Atom Transfer Radical Addition/Polymerization of Perfluorosulfonic Acid Polymer with the C−F Bonds as Reactive Sites

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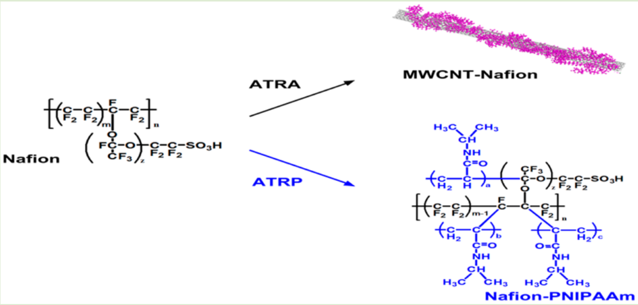
Supporting Information

ABSTRACT: This work reports the first demonstration of the chemical reactions on the C−F groups of perfluorosulfonic acid polymers. The Nafion chains show chemical reactivity for atom transfer radical addition onto multiwalled carbon nanotubes and ability to serve as a macroinitiator for atom transfer radical polymerization. The C−F groups and mainchain $-CF_2$ groups have been demonstrated, under a study with ^{19}F NMR, as the active sites responsible for the reactions. The results could certainly extend both the scopes of chemistry and application of perfluorosulfonic acid polymers as well as the windows of atom transfer radical addition/polymerization to fluorinated compounds.



Perfluorosulfonic acid polymers, like Nafion, have been widely utilized as proton exchange membranes (PEM) for fuel cells. The polymers exhibit high chemical resistance and mechanical stability basing on their perfluorinated chemistry. Nevertheless, the chemical inertness of the perfluorosulfonic acid polymers limits much on their reaction, modification, and functionalization as well as their extended windows of properties and application scopes. The inherently reactive sites for the polymers are the sulfonic acid groups. Hence, the reaction between Nafion sulfonyl fluoride precursor and tertiary amine compounds has been reported[1−4] for preparation of anion-exchange membranes. Our previous papers[5,6] reported that ozone-treatment could generate chemically reactive groups on Nafion chains, so as to chemically incorporate Nafion chains onto the outer surfaces of carbon nanotubes[5] and electrospun polymeric nanofibers.[6] The reaction has been attributed to the generation of hydroxide and peroxide groups on the Nafion chains. Chain scissoring might occur in the ozone treatment process.[7] Iwai et al.[8] reported radiation-induced cross-linking of Nafion-based membranes. Nevertheless, the reaction mechanism of Nafion chains in the ozone-mediated and radiation-induced process has not been well illustrated. Performance of well-defined and controllable chemical reactions on perfluorosulfonic acid polymers so as to prepare their functional derivatives is highly attractive and still not achieved.

Atom transfer radical addition/polymerization (ATRA/ATRP) usually involves C−Br or C−Cl groups as the reactive/initiating groups.[9−11] Meanwhile, the activity of C−F groups to initiate ATRP has been demonstrated,[12−18] although fluorine is usually considered as a bad leaving group in ATRP. For example, poly(vinylidene difluoride) (PVDF) has been utilized as a macroinitiator of ATRP with their C−F groups as the active sites.[12−17] The other example is hydrogen plasma-treated poly(tetrafluoroethylene) (PTFE) film.[18] Plasma treatment performs defluorination and hydrogenation reactions on the PTFE film surface, so as to change the chemical environment of the C−F groups to be PVDF-like and activate their ability to initiate ATRP. The developed chemistry provides easy approaches to prepare copolymers[12,13] and surface-modified films[14−19] of the fluoropolymers and extends the application scopes of the corresponding products.

The state-of-the-art is performance of ATRP initiated with the C−F groups of PVDF and PVDF-like polymers. More examples of ATRA/ATRP which is initiated with the C−F group of other fluoropolymers, for exmaple of perfluorosulfonic acid polymers, are worthy of studies. As the bond dissociation energies (BDE) of the C−F bonds of perfluorosulfonic acid polymers fall in a wide range of values,[20−22] the C−F groups which possess relatively low BDE might be more reactive than the others and could be able to initiate ATRP. As a result, in this work we demonstrate the first example to perform the chemical modification/functionalization of perfluorosulfonic acid polymers with ATRA/ATRP reaction (Figure 1). The results reported in this work develop new chemical reaction routes for perfluorosulfonic acid polymers, which is highly attractive both for the chemistry of ATRA/ATRP and the extended properties and application scopes of perfluorosulfonic acid polymers.

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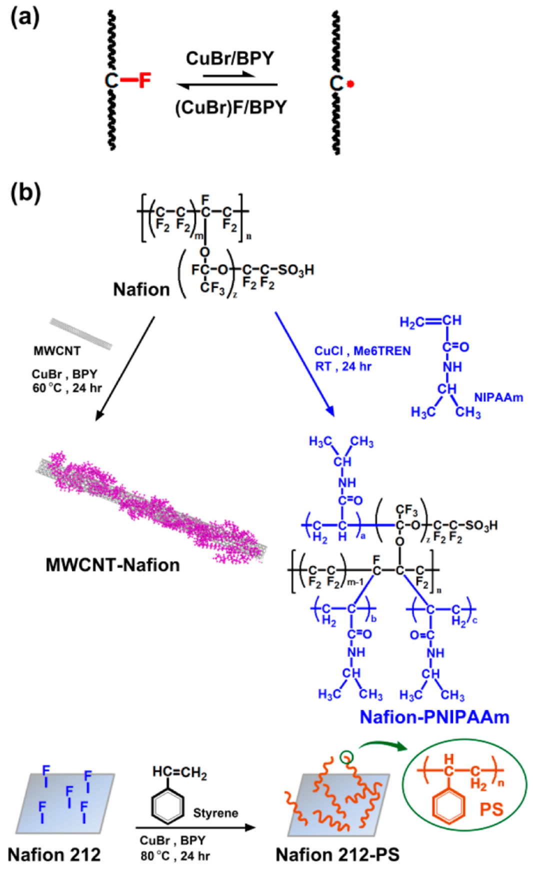


Figure 1. (a) Activation of Nafion chains for ATRA/ATRP reaction; (b) Reactions of Nafion chains: ATRA to MWCNT bundles to result in MWCNT-Nafion hybrids, ATRP of NIPAAm to generate Nafion graft copolymer of Nafion-PNIPAAm, and surface-initiated ATRP of styrene from Nafion 212 membrane.

As the ATRA reactions of C−Br[10] and C−F groups[19] have been reported, the ATRA reaction of Nafion chains is first examined with the ATRA-mediated incorporation of polymer chains to multiwalled carbon nanotubes (MWCNTs). A polymer chain possesses ATRA active groups could chemically react onto the outer surface of MWCNTs in the presence of effective catalysts and ligands. Several polymers, such as polystyrene,[23] poly(phenylene oxide) (PPO),[24] and polysulfone,[25] have been chemically incorporated onto the outer surfaces of MWCNTs so as to result in the corresponding MWCNT−polymer nanohybrids. Based on the similar chemistry, Nafion chains have been successfully reacted onto MWCNT surfaces through ATRA reaction with the C−F groups of Nafion chains as the reactive sites. The corresponding Nafion-functionalized MWCNTs (MWCNT-Nafion) have been obtained (Figure 1). The obtained MWCNT-Nafion has been characterized with FTIR, Raman, and XPS spectroscopies (Figures 2 and S1). The characteristic absorptions associating to the structure of Nafion in the FTIR spectrum (C−F at 1206 and 1143 cm^{-1}, $-SO_3H$ at 1051 cm^{-1}) and the appearance of S and F signals in the wide-scanning XPS spectrum of MWCNT-Nafion support to the presence of Nafion chains in the obtained MWCNT-Nafion sample. The increased ratio of D band over G band absorption in the Raman spectrum (from 0.64 to 0.89) indicates the performance of chemical reaction between Nafion chains and MWCNTs. Reaction between MWCNT and Nafion also results in an increase in the intensity of D′ band at about 1614 cm^{-1} (D′ band is directly affected by the disorder in nanotubes).[26] The fraction of Nafion in MWCNT-Nafion, determined with a thermogravimetric analysis (TGA) method (Figure S1), is about 50.4 wt %. The weight fraction of the grafted Nafion is comparable to the value reported to MWCNT-PPO prepared with the similar ATRA manner.[23] The micrograph of MWCNT-Nafion, recorded with a high-resolution transmission electron microscopy (HRTEM), shows the thickness of Nafion layer wrapped on the MWCNT outer surface is about 1.2 nm. Moreover, the dark regions in the HRTEM micrograph of the Pb-stained MWCNT-Nafion (with lead(II) acetate) correspond to the sulfonic acid domains of Nafion. The result supports to that Nafion chains cover on the outer surface of MWCNTs and the microphase-separation behavior of the Nafion portion. The size of the sulfonic acid domains is about 1−2 nm, which is smaller than the domain

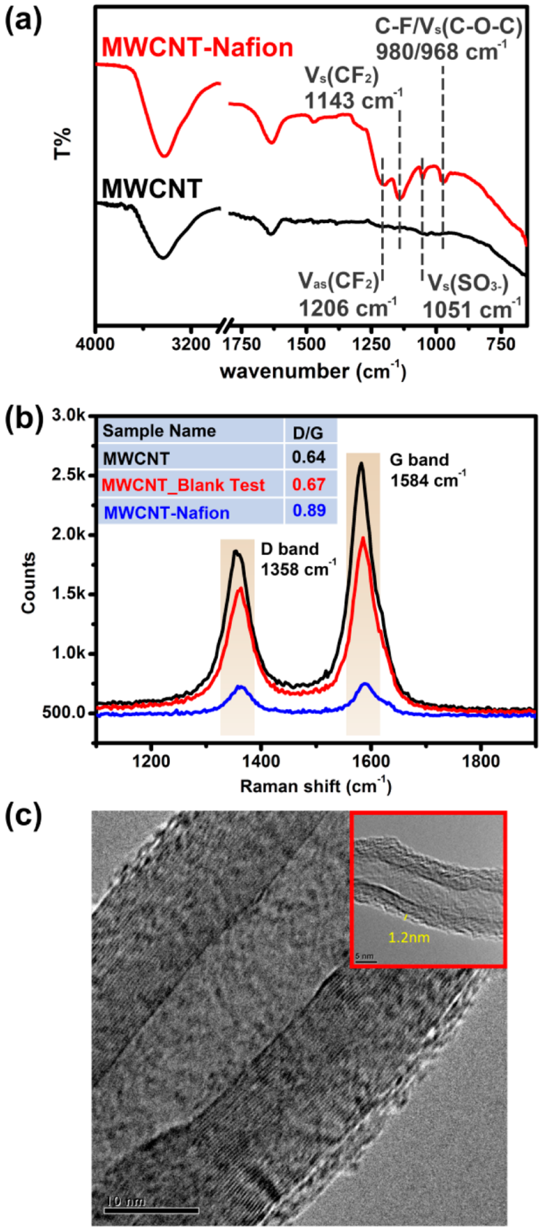


Figure 2. Characterization of Nafion-functionalized MWCNTs (MWCNT-Nafion) with (a) FTIR, (b) Raman spectroscopy, and (c) pb-stained high-resolution TEM (micrograph of the nonstained sample shown in as the inset micrograph) .

sizes observed with plain Nafion membranes as the Nafion portion of MWCNT-Nafion is in a confined environment. A control test, in which CuBr (the catalyst for ATRA reaction) was not added to the reaction system, was carried out. No obvious Nafion chains were observed to graft onto the MWCNT product obtained in control test. In the Raman analysis (Figure 2b), the MWCNT product in the control test did not exhibit an obvious D′ band and showed a D/G ratio of about 0.67 m, which is almost the same with the value (0.64) of the pristine MWCNTs. The results indicate that no chemical reactions performed on MWCNTs in the control test. It could be concluded here that the Nafion chains have been chemically reacted onto MWCNT bundles to result in the MWCNT-Nafion hybrid material. The obtained MWCNT−Nafion hybrid material could be used as a modifier for Nafion-based membranes to increase their proton conductivities.[5]

The reactivity of Nafion chains has been further examined with an ATRP using *N*-isopropylacrylamide (NIPAAm) as a monomer. The C−F groups of Nafion chains are proposed to serve as the active sites to initiate the ATRP of NIPAAm. To our best knowledge, the obtained product, coded as Nafion-PNIPAAm, is the first example of side-chain grafted Nafion copolymers. Nafion-PNIPAAm has also been spectrally characterized (Figures S2). In FTIR analysis, Nafion-PNIPAAm not only exhibits the specific absorptions arising from the Nafion chains but also the absorption peaks of PNIPAAm chains, including the peaks of −C═O at 1706 cm^{-1} and the peaks of amide groups at 1672 and 1540 cm^{-1}. Moreover, the results read from the C_{1s} core-level XPS spectrum of Nafion-PNIPAAm provides further supports to that the sample possesses both segments of Nafion and PNIPAAm chains. In addition to the characteristic peaks corresponding to the fluoride-containing groups at binding energy of about 289.4 to 293.7 eV ($-CFSO_3^-$, $-CF_2-$, and $-CF_3$), the appearance of the peaks at binding energy of 284.6 (C−H), 285.0 (C−C), 285.6 (C−C═O), 286.5 (C−O), 286.9 (C−N), and 287.7 (N−C═O) eV demonstrates the presence of PNIPAAm chains. The repeating unit ratio (Nafion/PNIPAAm) of Nafion-PNIPAAm, which has been determined with the F/C atom ratio of the sample (read from XPS analysis), is about 15, corresponding to a 7.7 wt % of PNIPAAm in the Nafion-PNIPAAm sample. The presence of PNIPAAm chains still alter the thermal degradation behavior of the sample in TGA measurement (Figure S3). Compared to the pristine Nafion sample, Nafion-PNIPAAm shows a relatively high thermal stability due to regarding the thermal degradation of the sulfonate groups of Nafion with formation of interchain hydrogen bonding between PNIPAAm and Nafion segments. It is noteworthy that some char yield has been found with Nafion-PNIPAAm at 800 °C. As both the neat Nafion and PNIPAAm samples do not show char residual in TGA measurements, some interaction between the Nafion and PNIPAAm chains might occur in the thermal degradation process to result in thermally stable nitrogen- and sulfur-containing char in the TGA measurement. Moreover, as PNIPAAm is a thermoresponsive polymer having a lower critical solution temperature (LCST) at about 32 °C, Nafion-PNIPAAm still exhibits a thermoresponsive behavior (Figure S4). Nevertheless, the LCST observed with Nafion-PNIPAAm shifts to about 13 °C as the PNIPAAm chains have been chemically bonded to the Nafion chains to reduce their solubility in water. To further verify the result, a mixture of Nafion and PNIPAAm homopolymer was prepared. The mixed product exhibited a LCST behavior that was similar to the LCST observed with the PNIPAAM homopolymer. The shift of the LCST of Nafion-PNIPAAm supports to that the PNIPAAm polymer is chemically bonded to the Nafion chains. Moreover, a control test for the graft polymerization, in which Nafion chains were not added to the reaction system, was also carried out. As there was not an initiator in the ATRP reaction system, polymerization of NIPAAm did not perform and no PNIPAAm was obtained. The result supports to that the PNIPAAm homopolymer could not form in the graft polymerization system and the obtained product should be the Nafion-PNIPAAm graft copolymer rather than the mixture of Nafion and PNIPAAm.

The ability of Nafion chains to serve as a macroinitiator for ATRP has been further examined with a surface-initiated ATRP from the commercial product of Nafion 212 membrane using styrene as a monomer. The obtained sample is coded as Nafion 212-PS. Similarly, PS homopolymer was not obtained in the control test, in which Nafion 212 membranes were not added to the reaction system. As a result, the observed PS chains could not be PS homopolymer physically absorbed on Nafion 212 and should be chemically tethered on the membrane surface. Surface characterization with an attenuated total reflectance FTIR (ATR-FTIR) and XPS have been performed (Figure S5). The chemically tethered PS chains show absorption peaks of $-CH_2$ groups at 2820 and 2849 cm^{-1} and phenyl groups at 1630 cm^{-1} in the ATR-FTIR spectrum of Nafion 212-PS. Moreover, the presence of PS chains on Nafion 212-PS surface was further characterized with the peaks at binding energy of 284.6 (C−H) and 285.0 (C−C) eV in the C_{1s} core-level XPS spectrum. Surface modification with PS also results in an increase in the surface hydrophobicity of Nafion 212 membrane, as the surface water contact angle of Nafion 212 increases from 96 to 105°, accompanied by PS modification. Finally, the surface morphology of Nafion 212 and Nafion 212-PS membranes have been observed with SEM. As shown in Figure 3, Nafion 212 shows a very smooth surface. After surface-initiated ATRP of styrene, the grafted PS chains result in a rough layer covering on the surafce of the Nafion 212-PS sample. The change in the surface morphology with the surafce-initiated ATRP supports to the successful incorporation of PS chains to Nafion 212 membrane surface.

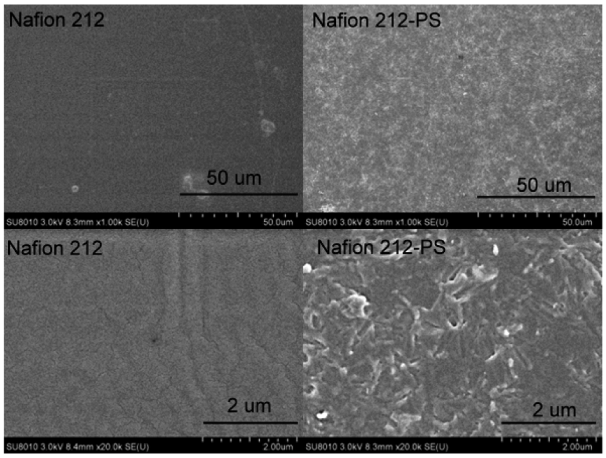
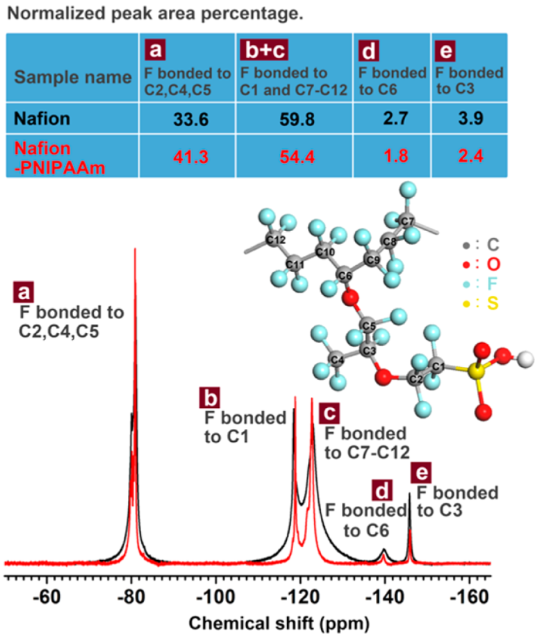


Figure 3. Surface SEM micrographs of Nafion and Nafion 212-PS membranes.

The ATRP of Nafion chains has been traced with ^{19}F NMR (Figure 4). Although Nafion and Nafion-PNIPAAm show similar resonance peaks in their ^{19}F NMR spectra, the relative integrated peak area ratios for some specific resonance peaks change with the ATRP reaction. The area normalization method has been used for the semiquantitative analysis. The ratio of the specific peak area to the total area of all peaks is taken as the relative concentration of the specific group. First, the relative signal intensity of peak **d** decreases from 2.7 to 1.8% based on the peak-area normalization method, indicating the C−F groups in the main segments (C6−F in Figure 3) of Nafion chains could be the active sites to initiate ATRP. This might be reasonable as the BDE of the C6−F groups has been calculated to be 435.6 kJ mol^{-1} according to the literature,[21] which is much lower than the general BDE (above 500 kJ mol^{-1}) calculated for most of the C−F bonds of Nafion chains. Moreover, the C3−F bond has a lowest BDE (455.6 kJ mol^{-1}) among the C−F bonds of the side segments of Nafion chains. The relatively low BDE of the C3−F group suggests its potential ability to involve in the ATRA/ATRP reactions. Reaction at the C3−F group might result in a decrease in the intensity of peak **e** in the ^{19}F NMR spectrum. This fact is supported with the experimental result, as the intensity ratio of peak **e** over peak **d** read for Nafion-PNIPAAm is smaller than the value read for Nafion. Ghassemzadeh et al.[27] studied the chemical degradation of perfluorosulfonic acid and concluded that the tertiary carbon C−F groups (C6−F groups at the mainchain and the C3−F at the side chains) of the polymer are relatively weak to be easily attacked with hydroxyl radicals. The results are coincident with what we have obtained in this work. On the other hand, the calculated BDE of C10−F2 bond is 435.4 kJ mol^{-1}.[21] As a result, the C10−F2 groups of Nafion could be another potential active sites for ATRA/ATRP reactions. This result might be supported with the decrease in the signal intensity of peak **c** in the ^{19}F NMR spectra. It is noteworthy that after initiation of ATRP, the $-C10F_2$ group changes to be −C10F− group, which has a similar chemical environment of C6−F and, consequently, contribute to the signal intensity of peak **d** in the ^{19}F NMR spectrum of Nafion-PNIPAAm. As the signal intensity of peak **d** decreases with the ATRP reaction, it could be concluded that the reactivity of C6−F group is higher than that of C10−F2 group. Based on the above discussion, it could be concluded that the active sites of Nafion chains to perform ATRA/ATRP reactions could be the C10−F2 and C6−F groups at the main chains and the C3−F group at the side chains. The activity of the tertiary carbon C−F groups (C6−F groups at the mainchain and the C3−F at the side chains) might be the dominant active sites for ATRA/ATRP reactions of Nafion chains.


Normalized peak area percentage.

Sample name	a F bonded to C2,C4,C5	b+c F bonded to C1 and C7-C12	d F bonded to C6	e F bonded to C3
Nafion	33.6	59.8	2.7	3.9
Nafion -PNIPAAm	41.3	54.4	1.8	2.4

Figure 4. ^{19}F NMR spectra of pristine Nafion and PNIPAAm-grafted Nafion (Nafion-PNIPAAm). The normalized peak area of specific resonance peaks in the attached table demonstrates the change of the chemical groups of Nafion chains in the graft polymerization.

Halogen exchange (HE) reaction in ATRP which employs the C−Cl and C−Br groups has been investigated.[28−31] Based on the results reported with Matyjaszewski et al.,[28] the fraction of C−Cl group of the terminal groups was about 80−90% in the ATRP reactions initiated with either R−Cl/Cu−Br or R−Br/CuCl compositions. As the C−F bond is less reactive compared to C−Cl and C−Br bonds, the possibility of HE from C−F to C−Br bond could be less in this work. We have carried out a preliminary examination to probe the possibility of HE reaction in this work, in which Nafion was reacted under the ATRP condition without addition of any monomers. The result shows that small amount of bromide could be detected (with an XPS, Figure S7) with the Nafion chains after the reaction. Nevertheless, as the HE reaction in the C−F initiated ATRP systems has not been quantitatively investigated, more studies might be of interest in the future work to probe the effect of the HE reaction on the kinetics of ATRP of Nafion and molecular weights of Nafion copolymers.

In conclusion, the reactivity of perfluorosulfonic acid polymers has been demonstrated with ATRA and ATRP reactions. The active sites for the reactions are the tertiary C−F groups at both the main and side segments of Nafion chains as well as the $-CF_2-$ groups next to the tertiary C−F linkages of the main chains. The ATRA reaction of Nafion is effective to incorporate functional chemical groups to Nafion chains for preparation of functional Nafion-based polymers, and the ATRP reaction is useful for preparation of graft copolymers of Nafion which have not ever been previously reported. The developments of the reactions of Nafion open a window to design and prepare new derivatives of perfluorosulfonic acid polymers, so as to extend the scopes of their properties and application fields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and characterization and property of Nafion-PNIPAAm graft copolymer and surface-modified Nafion 212-PS membrane. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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