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Se Hye Kim
University of Nevada, Las Vegas

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POST-MODIFICATION OF POLYSULFONE USING TRANSITION METAL CATALYZED C-H ACTIVATION AND SUZUKI–MIYAURA CROSS COUPLING REACTION

by

Se Hye Kim

Bachelor of Science
Ewha Womans University
2002

Master of Science
Ewha Womans University
2004

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Chemistry
Department of Chemistry
College of Sciences

Graduate College
University of Nevada, Las Vegas
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Se Hye Kim

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Dean of the Graduate College

Examination Committee Member

Examination Committee Member

Graduate College Faculty Representative

1017-53

ABSTRACT

Post-Modification of Polysulfone Using Transition Metal Catalyzed C–H Activation and Suzuki–Miyaura Cross Coupling Reaction

by

Se Hye Kim

Dr. Chulsung Bae, Examination Committee Chair
Assistant Professor of Chemistry
University of Nevada, Las Vegas

Polysulfone is a widely used high-performance engineering plastic because of its good mechanical and chemical stabilities. Even though polysulfone has excellent overall properties, the hydrophobic nature of the polymer precludes its broader use in membrane application where hydrophilic character is desired. Until now four post-modification methods of polysulfone have been reported: electrophilic sulfonation, chloromethylation, phthalimidomethylation, and lithiation with *n*-butyl lithium. However, all these methods suffer serious side reactions, such as chain cleavage and crosslinking of polymer chains, which can alter mechanical properties of the resulting polymer. We have developed a new post-functionalization method of polysulfone that utilizes transition metal catalyzed activation/functionalization of aromatic C–H bond. Based on viscosity measurement of the functionalized polysulfones, this new method does not result in negative effects on the polymer chain length. In addition, the pinacol boronic ester group that was installed on the polysulfone from the iridium-catalyzed aromatic C–H bond activation/functionalization can be converted to various polar functional groups,

including ketone, siloxy, sulfonated ester, and amine, via one-step Suzuki-Miyaura coupling reaction.

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CHAPTER 1

INTRODUCTION

1.1. Polysulfone

Udel® Polysulfone is a high-performance engineering plastic that has excellent high temperature stability (T_g = 190 °C) with a continuous use temperature of 150 °C and maximum use temperature of 170 °C. Polysulfone is also widely used as a membrane material for liquid and gas separation because of its semipermeable nature.[1] Despite its excellent thermal and mechanical properties, hydrophobic and nonpolar natures of polysulfone have precludes its applications in membrane separation where hydrophilic and polar characters are desired. Thus, the synthesis of functionalized polysulfone that can overcome its nonpolar character has been actively researched to broaden polysulfone's applications in material science and membrane technology. For example, sulfonated polysulfone is currently one of the best examples of a hydrocarbon based fuel cell membrane with comparable performance to that of Nafion. [2]

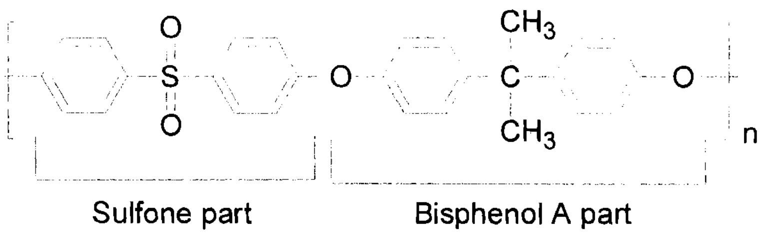


Figure 1. Chemical structure of polysulfone.

1.2. Existing post-modification methods of polysulfone

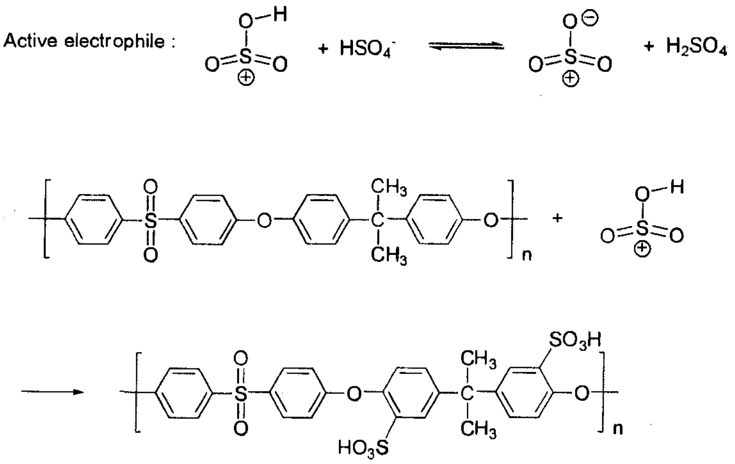
To introduce various functionalities into polysulfone, researches have used either copolymerization with functionalized comonomer or post-modification of the polymer. Although various functionalized comonomers, either dichlorosulfone or bisphenol A monomers, have been used for the polycondensation in the latter method to introduce functional group into polysulfone, the reduced reactivity of the functionalized monomer in the polymerization frequently resulted in the functionalized polysulfone as a low molecular weight polymer. In addition, the different reactivity of the functionalized comonomer could also cause a non-uniform distribution of functional groups in the polymer chain.

In the latter method, (homogeneous) post-modification of a polymer can in principle allow a uniform installation of a functional group along the polymer chain[1] and the degree of functionalization can be controlled simply by changing stoichiometry of the reactants.[3] Unfortunately, post-modification of polymer frequently causes undesirable side reactions which can alter the polymer chain length (i.e., chain scission and crosslinking) and thereby change the properties of the material. The excellent chemical stability of polysulfone poses even more challenges for post-modification of the polymer.

Thus until now, only handful examples of post-modification of polysulfone have been reported and they will be briefly described in the following sections.

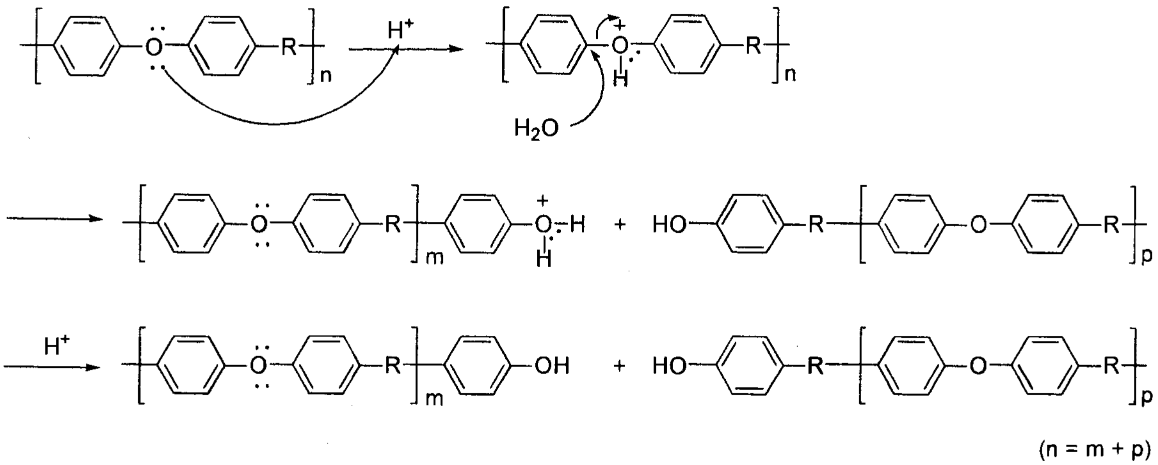
1.2.1. Electrophilic sulfonation of polysulfone

Electrophilic sulfonation is one of the most well studied electrophilic aromatic substitution reactions in organic chemistry. Because sulfonic acid group is an electron withdrawing deactivating group in electrophilic aromatic substitution, once one sulfonic acid group is introduced into the aromatic ring, the second incorporation of sulfonic acid group is more difficult, resulting in mostly monosulfonated aromatic ring. Because polysulfone consists of an electron rich bisphenol A unit and an electron deficient aryl sulfone unit (see Figure 1), two sulfonic acid groups can be incorporated to the (more electron rich) aromatic rings of the bisphenol A unit (Scheme 1). Sulfonation takes place at the ortho position of phenyl ether due to the electrophilic effect of the ether linkage toward electrophilic aromatic substitution. Reagents commonly used for the sulfonation are fuming sulfuric acid, concentrated sulfuric acid, and chlorosulfonic acid, which can be used as both a reagent and as a solvent.



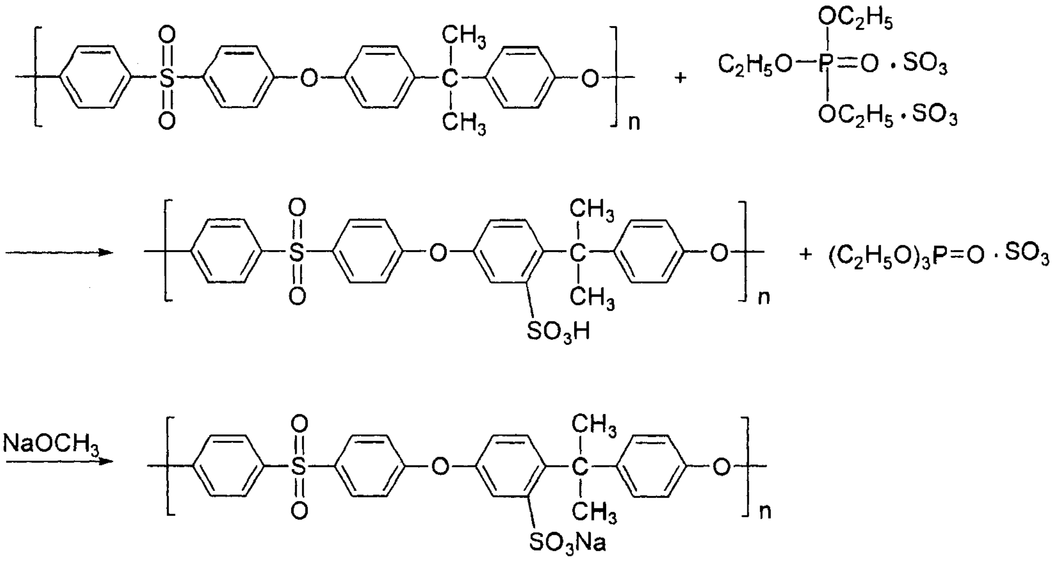
Scheme 1. Electrophilic sulfonation of polysulfone.

However, the sulfonation reagents mentioned above are extremely reactive and often cause undesired side reactions, such as polymer degradation. In a plausible mechanism, the aryl ether linkage of polysulfone is protonated under the strongly acidic condition and the ipso carbon in the aromatic ring is attacked by a nucleophile (e.g., H_2O), breaking the C–O bond (Scheme 2).[4]



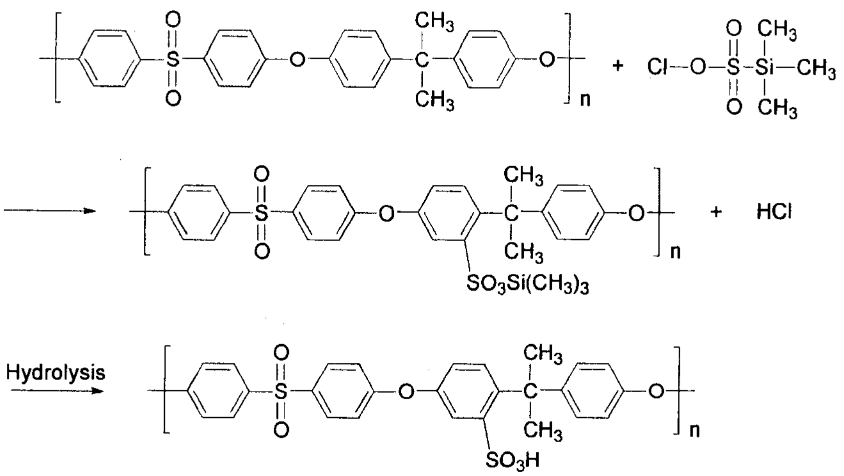
Scheme 2. A plausible chain degradation mechanism of polysulfone by acid-catalyzed hydrolysis.

SO_3 is an appealing inexpensive sulfonation reagent, however, it is extremely reactive and causes the undesirable side reactions during polymer sulfonation. Thus, a complexation with triethylphosphine, which can mitigate the high reactivity of SO_3, has been adopted.[5] When this SO_3-triethylphosphate was used in sulfonation of polysulfone in dichloroethane solvent, although still induces very exothermic reaction, it could reduce the reactivity of SO_3 and gave more predictable sulfonation results with less side reactions (Scheme 3). However, the complexation still requires the use of highly toxic SO_3, making it less attractive for practical use.[6]



Scheme 3. Electrophilic sulfonation of polysulfone using SO$_3$-triethylphosphate.

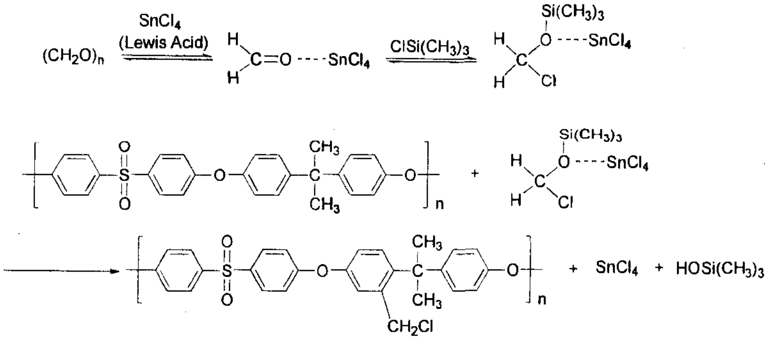
Another major drawback of sulfonation is partial precipitation of the polymer during the sulfonation reaction. Due to the dramatic difference in solubility between polysulfone and sulfonated polysulfone, the reaction medium is not homogeneous and may result in partial precipitation of the sulfonated polymer from the organic solvent. To overcome the partial precipitation problem of the sulfonation of aromatic polymers, a new sulfonation method using trimethylsilyl chlorosulfonate has been reported (Scheme 4).[7] The incorporated trimethylsilysulfonate group maintains the hydrophobicity of polysulfone, allowing for a homogeneous reaction mixture throughout the sulfonation reaction. Because of reduced reactivity of trimethylsilyl chlorosulfonate compared to that of chlorosulfonic acid, this hydrophobic sulfonating reagent can reduce the possibility of polymer degradation during the sulfonation. Once the trimethylsilylsulfonate group is successfully incorporated into polysulfone chain, it can be converted to a sulfonic acid group via hydrolysis of trimethylsilyl group (Scheme 4).



Scheme 4. Sulfonation of polysulfone using trimethylsilyl chlorosulfonate.

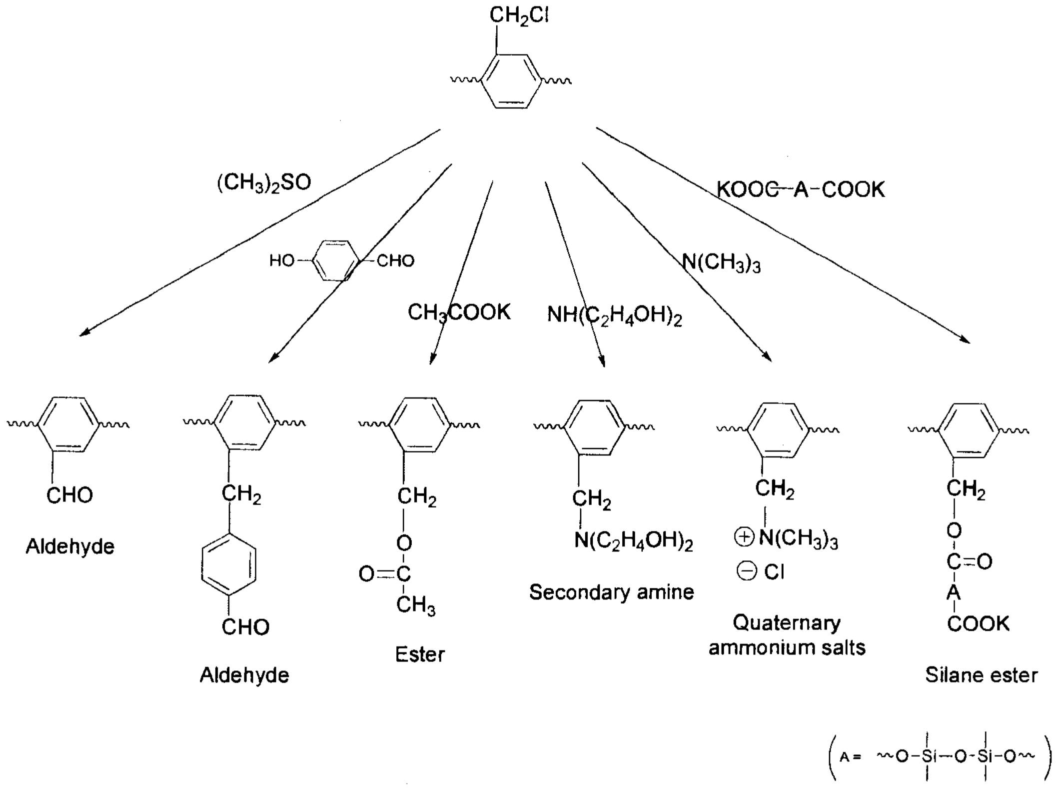
1.2.2. Chloromethylation of polysulfone

Chloromethylation is an electrophilic aromatic substitution reaction that requires an acid catalyst and a Lewis acid for generation of chloromethyl cation,[8] the active electrophile of chloromethylation. The chloromethyl cation is generated from mixture of paraformaldehyde and chlorotrimethylsilane in the presence of a Lewis acid catalyst (Scheme 5).[9] The active cation reacts with the electron rich bisphenol A aromatic rings of polysulfone and incorporates a chloromethyl group, which can be further transformed to various functional groups via a nucleophilic substitution reaction (i.e., S_N2 reaction).



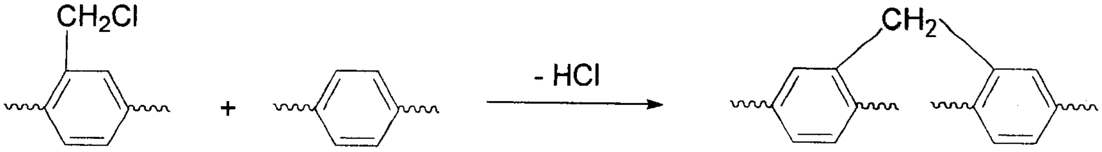
Scheme 5. Synthesis of chloromethylated polysulfone using chloromethylation reagent.

Chloromethylated polysulfone has been used as an intermediate in the introduction of various functional groups. By reacting with a variety of nucleophiles, polysulfones functionalized with aldehyde,[8] ester,[8] secondary amine,[8] quaternary ammonium salts, [8] and silane ester substituents[10] have been prepared. (Scheme 6)



Scheme 6. Synthesis of various functionalized polysulfones from the chloromethylated intermediate polymer.

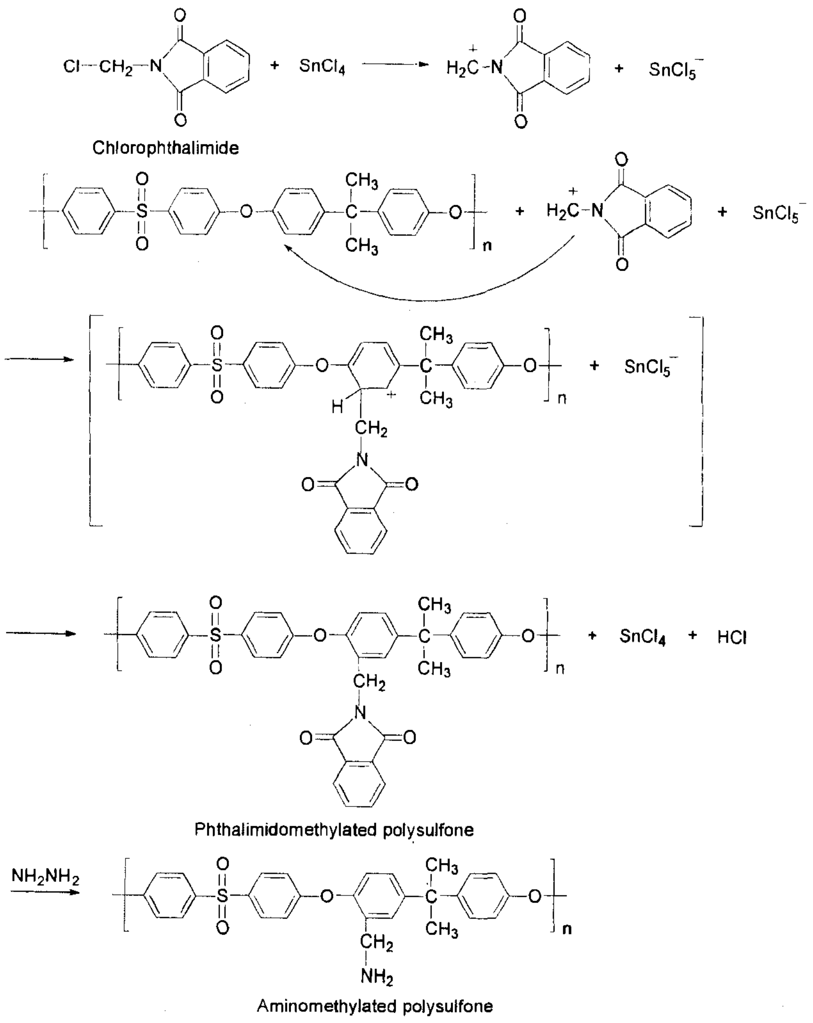
Although chloromethylated polysulfone has been used as an intermediate for the generation of functionalized polysulfones, the degree of chloromethylation is not easily controllable as seen in the electrophilic sulfonation reaction and generally causes polymer cross-linking by forming methylene bridge. (Scheme 7) [11,12]



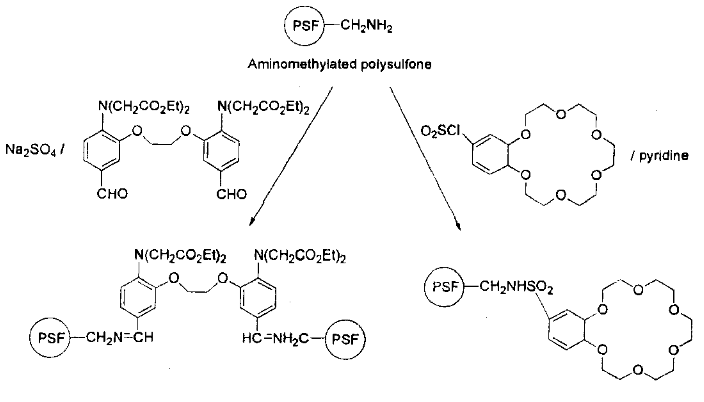
Scheme 7. Cross-linking mechanism of chloromethylated polysulfone.

1.2.3. Aminomethylation of polysulfone

Phthalimidomethylated polysulfone, which can be converted to aminomethylated polysulfone, was prepared via an electrophilic aromatic substitution (Scheme 8). Chlorophthalimide was treated with $SnCl_4$ to generate the active phthalimidomethyl cation, which can react with the electron rich aromatic ring of polysulfone via electrophilic aromatic substitution reaction. The degree of functionalization up to 0.8 could be achieved with this route. When more effective Lew acid catalyst such as $AlCl_3$ and $FeCl_3$ were used instead of $SnCl_4$, higher degree of funcitonalization could be achieved (degree of functionalization up to 1.45 for $AlCl_3$).[8] The subsequent hydrazinolysis with NH_2NH_2 gave aminomethylated polysulfone, which can serve as an intermediate for various funcitonalized polysulfones (Scheme 9). Warshawsky and co-workers have reported the detailed study of aminomethylated polysulfone and its membrane applications in selective alkali ion adsorption.[13, 14] In general, the degree of functionalization is not easy to control as seen in other acid catalyzed reactions such as chloromethylation of polysulfone.



Scheme 8. Preparation of the aminomethylated polysulfone.



Scheme 9. Synthesis of various functionalized polysulfones from the aminomethylated intermediate polysulfone.

1.2.4. Metallation of polysulfone

Guiver and co-workers reported the post-modification of polysulfone using a direct lithiation procedure[15] and a bromination-lithiation procedure.[16] The direct lithiation method allows the functional group to be installed at the ortho position of the electron deficient sulfone aromatic ring of polysulfone due to the powerful directing ability of the oxygen in the sulfone group of the polymer (Figure 2). Accordingly, this direct lithiation reaction is highly regioselective. The lithiated polysulfone intermediate, which was generated in situ, was further reacted with a variety of electrophiles to incorporate various functional groups. (Scheme 10)

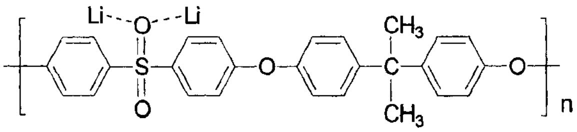
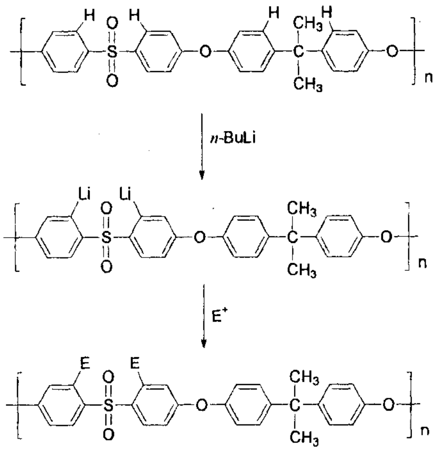
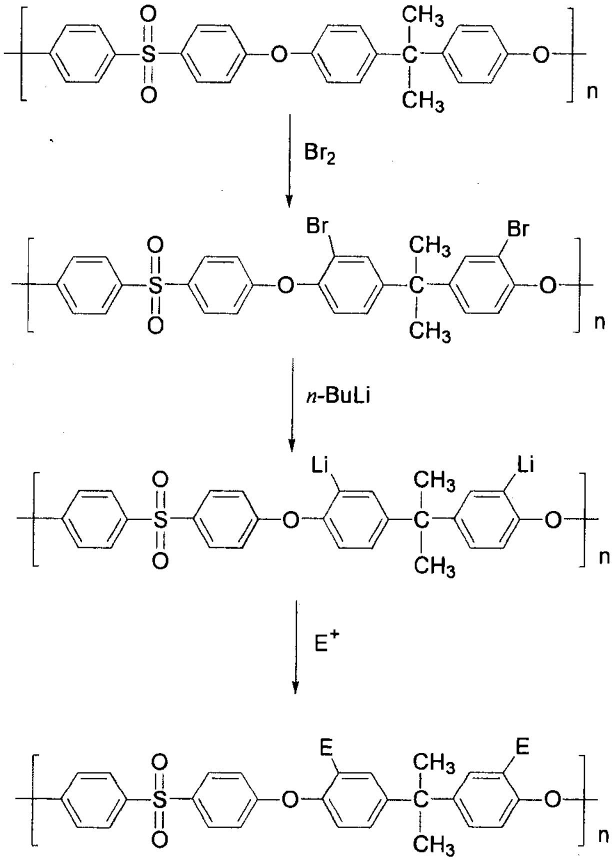


Figure 2. Regioselective direct lithiation of polysulfone: lithium is coordinated to the oxygen atom of the sulfone group.



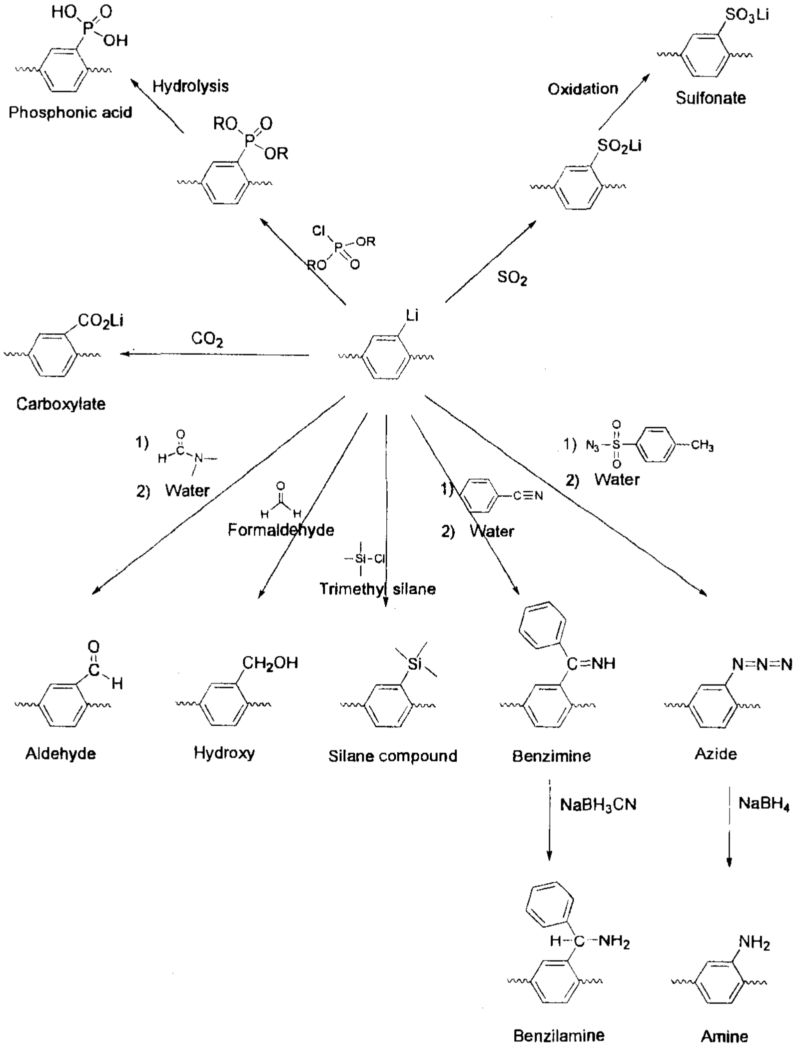
Scheme 10. Polysulfone functionalization via direct lithiation followed by reactions with electrophiles. (E^+ = Electrophile)

In contrast, bromination-lithiation of polysulfone allows functionalization at the electron rich aromatic ring (i.e., bisphenol A ring) of polysulfone. (Scheme 11) Since the bromination proceeds through an electrophilic aromatic substitution pathway, the ortho position of the aryl ether linkage is the most favorable site for the bromination. After bromination, the bromine can be replaced with lithium via a halogen-metal exchange reaction at low temperatures (i.e., –78 °C). The resulting lithiated polysulfone, like the one from the direct lithiation route, was further reacted with different electrophiles to form various functionalized polymers. (Scheme 11)



Scheme 11. Functionalization of polysulfone via bromination-lithiation process. (E$^+$ = Electrophile)

Both modification methods shown above generated the lithiated polysulfone intermediates in-situ, which were subsequently reacted with a variety of electrophiles. By reacting with various electrophiles, polysulfones functionalized with carboxylate,[17] hydroxyl, [18] azide, [19] primary amine, [20] aldehyde, [21] dipyridyl, [22] silicon, [1, 23], phosphonic acid, [24] sulfonate, [25] benzimine, [3] and benzylamine substituents[3] have been prepared (Scheme 12).



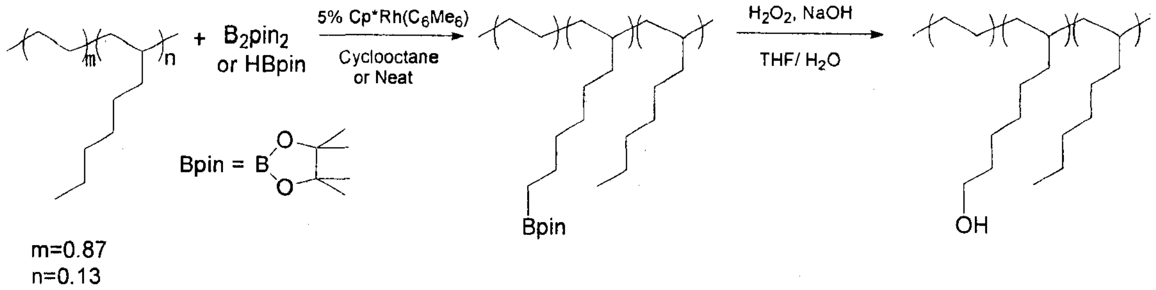
Scheme 12. Synthesis of various functionalized polysulfones from the lithiated intermediate polymer.

However, the metallation process requires a highly reactive lithium reagent (i.e., *n*-BuLi), which can cause cross-linking in the polymer. In addition, because the metallation requires perfectly anhydrous inert conditions and low temperatures (–78 °C to –50 °C), this functionalization method seems to be difficult to adopt in a large-scale process.

1.3. New post-modification of polysulfone using C–H activation/functionalization

1.3.1. Functionalization of polymer via transition metal catalyzed activation/functionalization of C–H bond

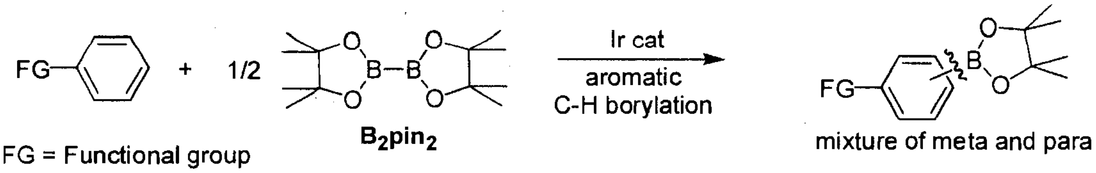
Transition metal catalyzed C–H bond activatio n/functionalization has recently emerged as a new method of polymer post-modification. Unlike traditional post-functionalization via reactive free radical or carbocation intermediates, where polymer degradation and chain cross-linking reactions pose a significant problem, the post-modification of polymer via transition metal catalyzed C–H functionalization shows only a negligible change in polymer's molecular weights. This new post-modification method, initially developed in order to introduce polar functional groups into saturated polyolefins, has been successfully adopted not only in amorphous polyolefins substrate[26] but also in crystalline saturated polyolefins.[27, 28] Unfortunately, when it was adopted for functionalization of high-molecular-weight semicrystalline polymers, it generated a relatively low concentration of polar functionality (Scheme 13).



Scheme 13. Regiospecific C—H bond activation/functionalization and subsequent oxidation of linear low-density polyethylene.[28]

1.3.2. Iridium-catalyzed activation/functionalization of aromatic C–H bond

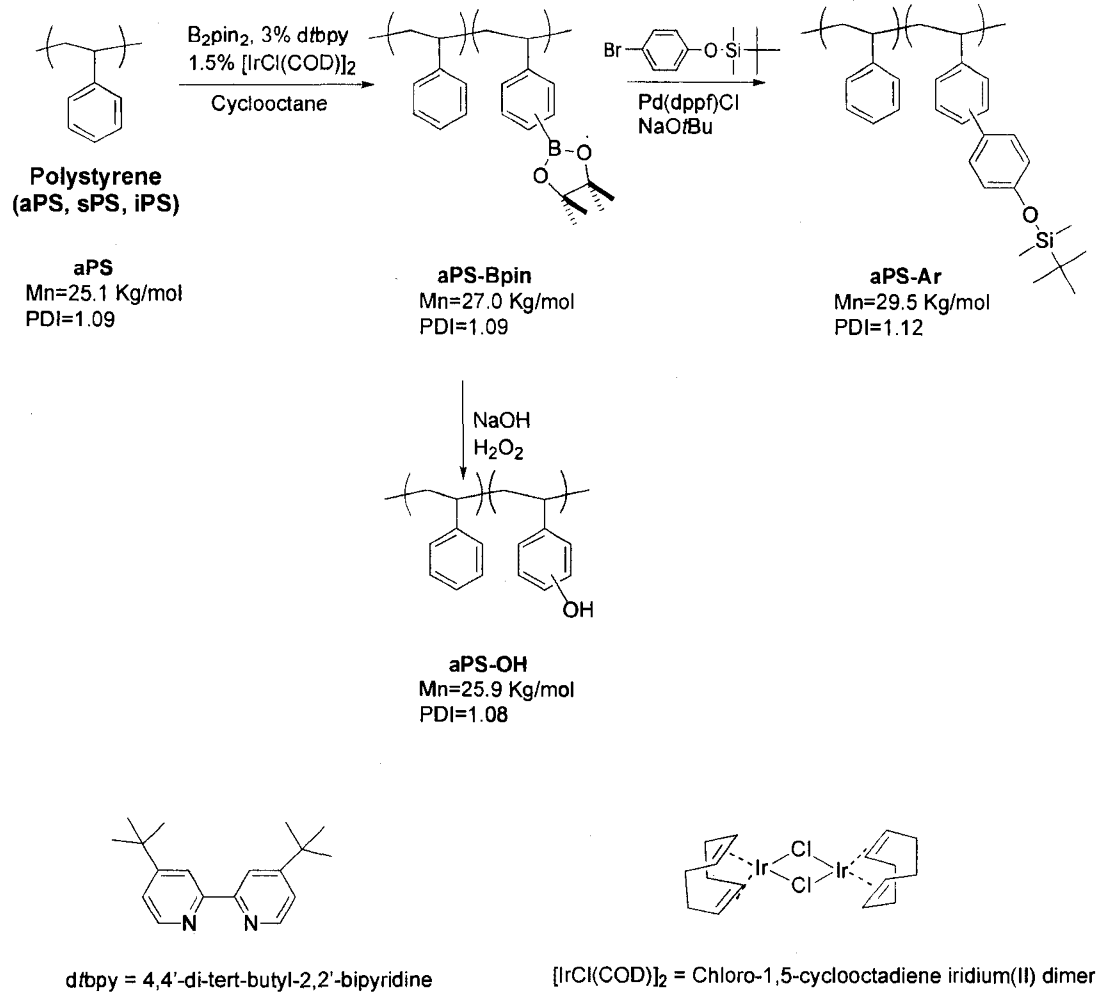
Generally, arylboron compounds have been prepared via transmetalation between aryllithium reagents and boron compounds.[29] Recently, a mild method for preparing arylboronic ester directly from arenes has been developed: the iridium-catalyzed aromatic C–H borylation of arenes (Scheme 14).[30, 31] Although electrophilic aromatic substitutions such as sulfonation and nitration are still common methods for introducing a functional group into an aromatic ring, they are less reactive toward electron-deficient aromatic rings. By contrast, the iridium–catalyzed aromatic C–H borylation shown in Scheme 14 is more reactive when the substituent in the aromatic ring is an electron-withdrawing group. For example, the aromatic C–H borylation of an equal mixture of trifluoromethylbenzene and toluene (FG = CF_3 and CH_3, respectively, in Scheme 14) generates the corresponding arylboronic esters in a ratio of 90:10, indicating that the electron-deficient aromatic ring is more reactive.[30] Additionally, unlike in electrophilic aromatic substitution, the regioselectivity in aromatic C–H borylation is governed *only* by the steric effect of a substituent—giving regioisomeric mixture of meta- and para-borylated products in a statistical ratio (ca. 2:1) for a monosubstituted benzene.[30]



Scheme 14. Iridium-catalyzed C–H borylation of arene.[30]

1.3.3. Iridium-catalyzed activation/functionalization of aromatic C–H bond in aromatic side-chain polymers

Bae and co-workers have recently reported the first example of iridium-catalyzed C–H bond activation/functionalization of aromatic side-chain polymers.[32] Polystyrenes with three different tacticities (atactic [aPS], isotactic [iPS], and syndiotactic [sPS]) were borylated using bis(pinacolato)diboron (B_2pin_2) and a commercial iridium catalyst (Scheme 15). The pinacol boronic ester (Bpin) group on the polystyrene was found to be a versatile intermediate group which can be converted to hydroxy and arene groups via oxidation and Suzuki-Miyaura coupling reaction, respectively. Similar to the iridium-catalyzed C–H bond activation/functionalization of monosubstituted arenes,[33] where only aromatic C–H bonds were borylated with a statistical mixture of ortho, meta, para in a ratio of 0:7:3, the same functionalization on polystyrene introduced Bpin group only at the aromatic ring of the polymer, without affecting the saturated polymer main-chain (Scheme 15). In contrast to previously known polystyrene post-modification process based on free radical or carbocation intermediates, the C–H borylation of aromatic ring of polystyrene was achieved with high efficiency without disrupting the tacticity and the polymer chain length, maintaining the original chain length of the precursor polymer.



Scheme 15. Iridium-catalyzed C–H bond activation/functionalization, subsequent oxidation, and Suzuki-Miyaura coupling reaction of polystyrenes. [32]

1.3.4. Iridium-catalyzed activation/functionalization of aromatic C–H bond in aromatic main-chain polymers: A new mild post-functionalization of polysulfone

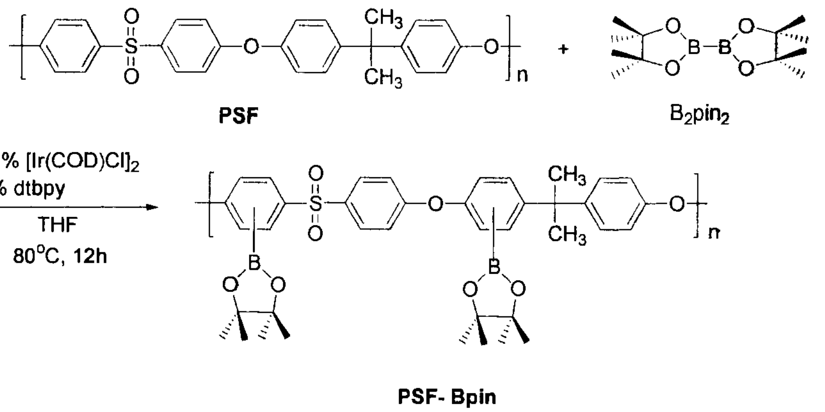
With this success on polystyrene post-modification in hand, we have decided to explore this new polymer modification method for aromatic main-chain polymer system. Post-functionalization of aromatic ring in a polymer main-chain is more difficult than that of polymer side-chain, because even a minute amount of side reactions that cleave the aromatic ring can result in a significant reduction in polymer chain length and degradation of mechanical strength. As mentioned earlier, polysulfone is an important engineering plastic and mild post-functionalization of polysulfone has not been reported until now. Thus, we have selected polysulfone as a polymer substrate to demonstrate effectiveness of the iridium-catalyzed C–H borylation in post-functionalization of aromatic main-chain polymers. As will be discussed in detail in the following chapters, we have developed the mildest post-functionalization of polysulfone that can be carried out even at room temperature without causing negative effects on the polymer chain length (i.e., neither chain scission nor cross-linking). In addition, the Bpin group on the polysulfone, which was installed from the iridium-catalyzed aromatic C–H bond activation/functionalization, can be converted to various polar functional groups including ketone, ester, sulfonate ester, sulfonic acid, amine, and ammonium salt via subsequent Suzuki-Miyaura coupling reaction with appropriate aryl bromides.

CHAPTER 2

RESULTS AND DISCUSSIONS

2.1. Iridium-catalyzed C–H borylation of Udel® polysulfone

The iridium-catalyzed C—H bond borylation of commercial Udel® polysulfone (PSF of Scheme 16) with different molar ratios of B_2pin_2 to polymer repeating unit was performed in tetrahydrofuran (THF) solvent and provided the corresponding borylated polysulfone product (PSF-Bpin of Scheme 16).



Scheme 16. Iridium-catalyzed borylation of C—H bond of aromatic rings of polysulfone.

The mol % of the attached Bpin group per polysulfone repeating unit was calculated by comparing the proton integrals of the two methyl groups of the isopropylene in the polysulfone main-chain and the four methyl groups of the Bpin in the

^{1}H NMR spectra of PSF-Bpin, and their values are summarized in Table 1. The mol % of Bpin attached to polysulfone increased from 41 to 186 mol % as the ratio of added B_2pin_2 to polymer repeating unit increased from 0.4 to 2.0 (entries 2–10 of Table 1). The efficiency of the C–H borylation is defined as the amount of Bpin attached to the polymer repeating unit per the amount of boron atom added. Except for entry 1, where no Bpin was incorporated under the condition, all ratios above 0.2 induced successful installation of Bpin group in polysulfone unit and their efficiencies of C–H functionalization were consistently 40–50%, which allows consistent degree of functionalization by stoichiometric tuning of the amount of added B_2pin_2. While the efficiency of C—H bond borylation in aromatic side chains of polystyrene was continuously decreased,[32] the efficiency of C—H bond borylation in aromatic main chain of polysulfone maintained approximately 40–50 %. Using this method, up to 186 mol % of the repeating unit of polysulfone could be funcitonalized with pinacol boronic ester group with high efficiency (entry 10 of Table 1).

For detailed studies of the functionalized polymers, the ^{1}H and ^{13}C NMR spectra of PSF—Bpins prepared from the ratio of 0.40 (40—PSF—Bpin) and 1.6 (160—PSF—Bpin) were examined (Figures 3 and 4). For comparison, ^{1}H and ^{13}C NMR spectra of unfunctionalized polysulfone are included in Figures 3a and 4a. Polysulfone has four different types of aromatic C–H bonds in the repeating unit; two in the sulfone unit and two in the bisphenol A unit (see Figure 1). Thus, the C–H borylation of polysulfone in principle can create four different regioisomers of Bpin-functionalized polymers possibly with an unequal distribution. As shown in Figure 3b, two proton resonances of the Bpin group of 40—PSF—Bpin (i.e., H_b of Figure 3b) appeared at 1.0 and 1.2 ppm, indicating the presence of two different types of regioisomers when a relatively low ratio of B_2pin_2 to repeating unit (i.e., ratio = 0.4) was added. The relative proton integral ratio of H_b of the Bpin and H_a of the isopropylidene group of polysulfone allowed estimation of the mol % of Bpin group in the polymer (41 mol % Bpin, entry 2 of Table 1). The 51 % efficiency of C–H functionalization was calculated by dividing the mol % of Bpin group by the mol amount of boron atoms added per repeating unit.

In the ^{1}H NMR spectrum of 160—PSF—Bpin, not only higher concentration of the methyl groups of the Bpin moiety in the polymer but also one additional small methyl peaks from the Bpin group appeared at 1.0–1.3 ppm (Figure 3c). Furthermore, the resonance of the isopropylene group in the polysulfone main-chain at 1.7 ppm was split as the ratio of added B_2pin_2 relative to the polymer's repeating unit increased from 0.40 to 1.6. The aromatic proton peaks at 6.5–8.0 ppm also displayed additional resonances as the concentration of the attached Bpin group increased.

As shown in Figure 4b–c, the Bpin groups in the borylated polymers showed two characteristic peaks in their ^{13}C NMR spectra at 24 ppm and 84 ppm, which corresponded to the four terminal methyl groups of the Bpin groups and the quaternary carbon of the Bpin group, respectively. Similar to the aromatic region of ^{1}H NMR spectra, the ^{13}C NMR spectra of the borylated polysulfones contained additional aromatic resonances at 110–170 ppm due to the presence of Bpin-functionalized aromatic rings.

Table 1. C–H bond activation/borylation of polysulfone (PSF) with bis(pinacolato)diboron (B_2pin_2) to generate pinacol boronic ester-functionalized polysulfone (PSF–Bpin).[a,b]

entry	$[B_2pin_2]$/ [PSF repeating unit][c]	PSF–Bpin	Bpin attached (mol %)[d]	Efficiency of C–H borylation (%)[e]
1	0.2	20–PSF–Bpin	0	0
2	0.4	40–PSF–Bpin	41	51
3	0.6	60–PSF–Bpin	56	47
4	0.8	80–PSF–Bpin	66	41
5	1.0	100–PSF–Bpin	86	43
6	1.2	120–PSF–Bpin	108	45
7	1.4	140–PSF–Bpin	128	46
8	1.6	160–PSF–Bpin	148	46
9	1.8	180–PSF–Bpin	179	50
10	2.0	200–PSF–Bpin	186	47

[a] Borylations were conducted with 133 mg of polysulfone in the presence of 1.5 mol % of $[IrCl(COD)]_2$ and 3 mol % of d*t*bpy relative to the amount of B_2pin_2 in 0.75 mL of THF at 80°C for 12h.

[b] PSF = polysulfone; Bpin = pinacol boronic ester

[c] The mol % of B_2pin_2 added relative to the repeating unit of polymer.

[d] The mol % of Bpin functionalized polysulfone unit calculated from the ^1H NMR spectra by comparing the proton integrals between two methyl groups of the isopropylene group of polysulfone main-chain and four methyl groups of Bpin attached to the polymer.

[e] Efficiency (%) of C–H borylation: the amount of Bpin attached to the polymer divided by the amount of boron atom added.

^{11}B NMR spectra of both 40–PSF–Bpin and 160–PSF–Bpin showed broad peaks at 30 ppm, which was in good agreement with the chemical shift of the pinicol boronic ester in borylated polystyrene.[32] As the mol % of Bpin groups in polymer increased, the intensity of boron peak also increased under the same concentration (Figure 5a–b).

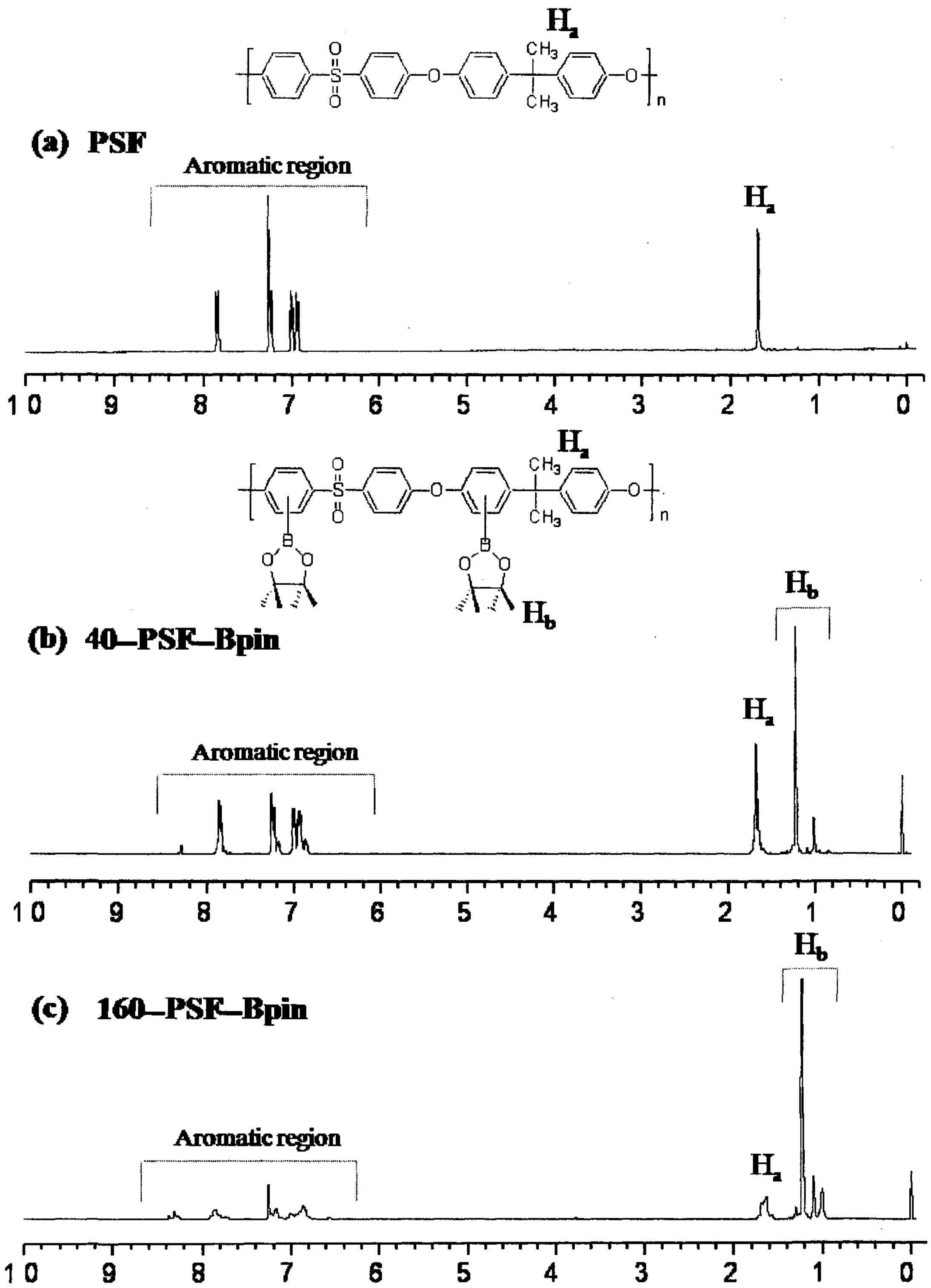


Figure 3. ^{1}H NMR spectra [delay time = 1s, number of transients = 16] of (a) PSF, (b) 40–PSF–Bpin, and (c) 160–PSF–Bpin [10 mg/mL in $CDCl_3$ at 25°C].

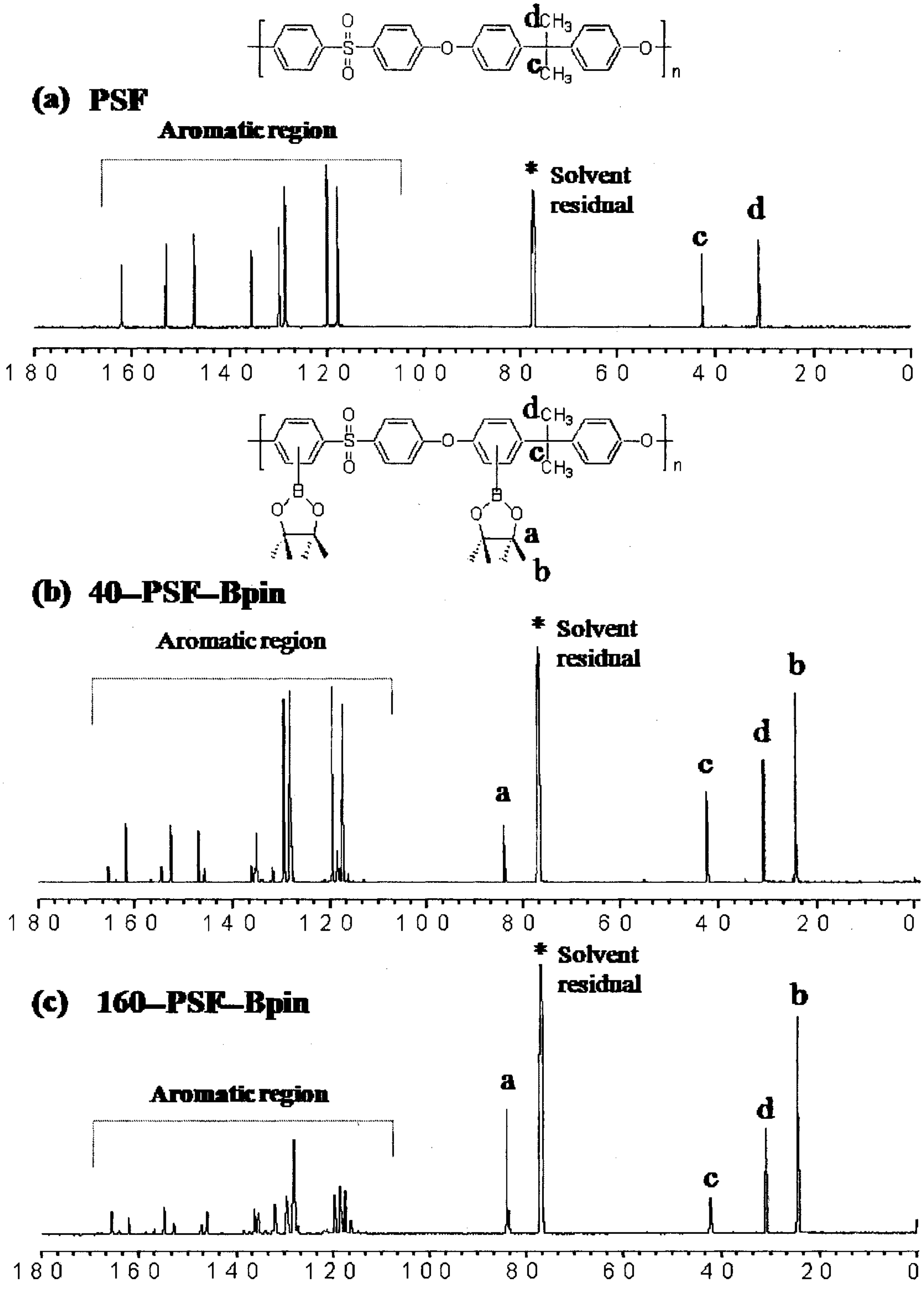
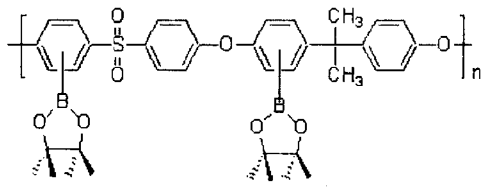
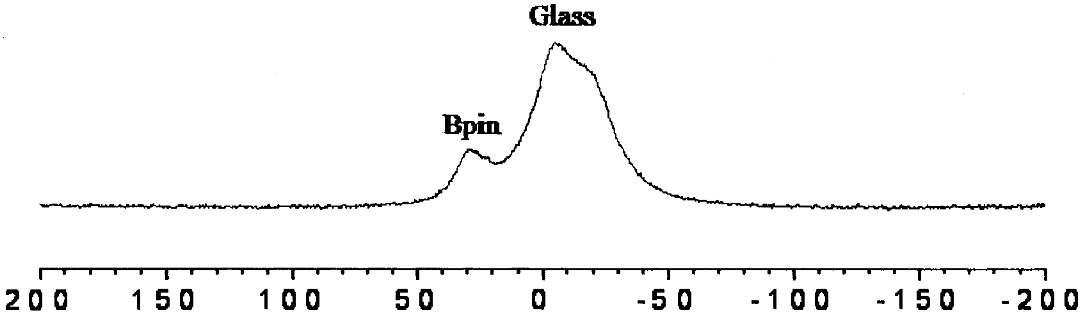


Figure 4. ^{13}C NMR spectra [delay time = 4s, number of transients = 8000] of (a) PSF, (b) 40–PSF–Bpin, and (c) 160–PSF–Bpin [40 mg/mL in $CDCl_3$ at 25°C].



(a) 40–PSF–Bpin



(b) 160–PSF–Bpin

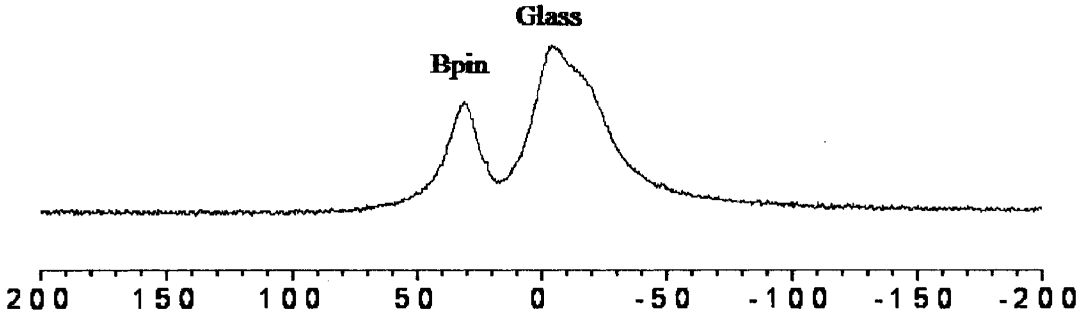
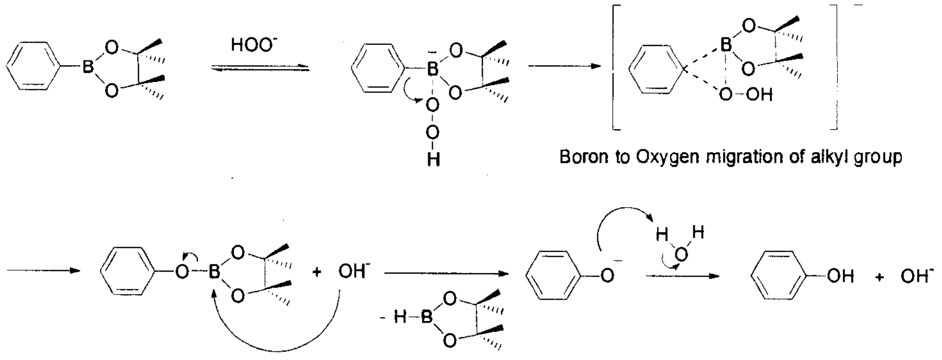


Figure 5. ^{11}B NMR spectra [delay time = 4s, number of transients = 100] of (a) 40–PSF–Bpin and (b) 160–PSF–Bpin [40 mg/mL in $CDCl_3$ at 25°C].

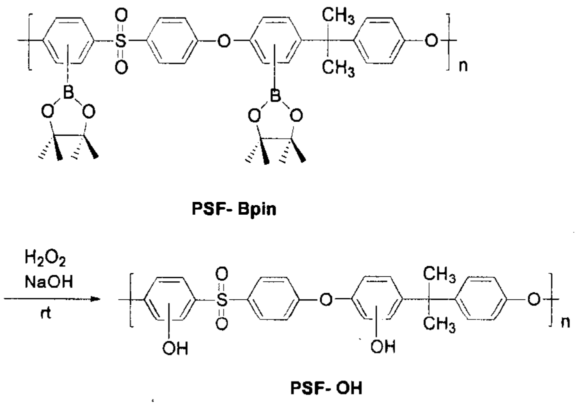
2.2. Oxidation of pinacol boronic ester group in the borylated polysulfone

The oxidation of the boronic ester to hydroxyl group is the most widely used reaction of organoboranes. It has been shown that the pinacol boronic ester could be oxidized to the corresponding alcohol in the presence of a base and hydrogen peroxide.[34] Scheme 17 illustrates the proposed mechanism of the oxidation.



Scheme 17. Mechanism of the oxidation of aryl pinacol boronic ester to alcohol.

Using this established protocol, we prepared hydroxyl-functionalized polysulfone (PSF-OH of Scheme 18) by oxidizing the Bpin group of PSF-Bpin with NaOH/H_2O_2 in a mixture of THF and H_2O (Scheme 18).



Scheme 18. Preparation of hydroxy-functionalized polysulfone by oxidation of pinacol boronic ester-functionalized polysulfone.

40-PSF-Bpin and 160-PSF-Bpin were converted to the corresponding hydroxylated polysulfones by oxidation (40-PSF-OH and 160-PSF-OH). Upon the oxidation, the hydroxy-functionalized polymers were not soluble in chloroform and THF, but soluble in polar aprotic solvent such as dimethylsufoxide (DMSO) and N,N'-dimethylacetamide (DMAc). The ^1H NMR spectra of the hydroxy-functionalized polysulfones obtained from a solution of DMSO-d_6 showed the resonances from the isopropylidene group and the aromatic protons of polymer main chain but the resonance of the Bpin disappeared (Figure 6a–b).

FT-IR spectra of the hydroxy-functionalized polysulfones showed a strong and broad O—H stretching band from the hydroxyl group at 3446 cm^{-1} for 40—PSF—OH (Figure 7a) and at 3433 cm^{-1} for 160—PSF—OH (Figure 7b). Both the ^1H NMR and IR spectra of 40—PSF—OH and 160—PSF—OH implied that the Bpin group of the borylated polymers was successfully converted to the hydroxyl group.

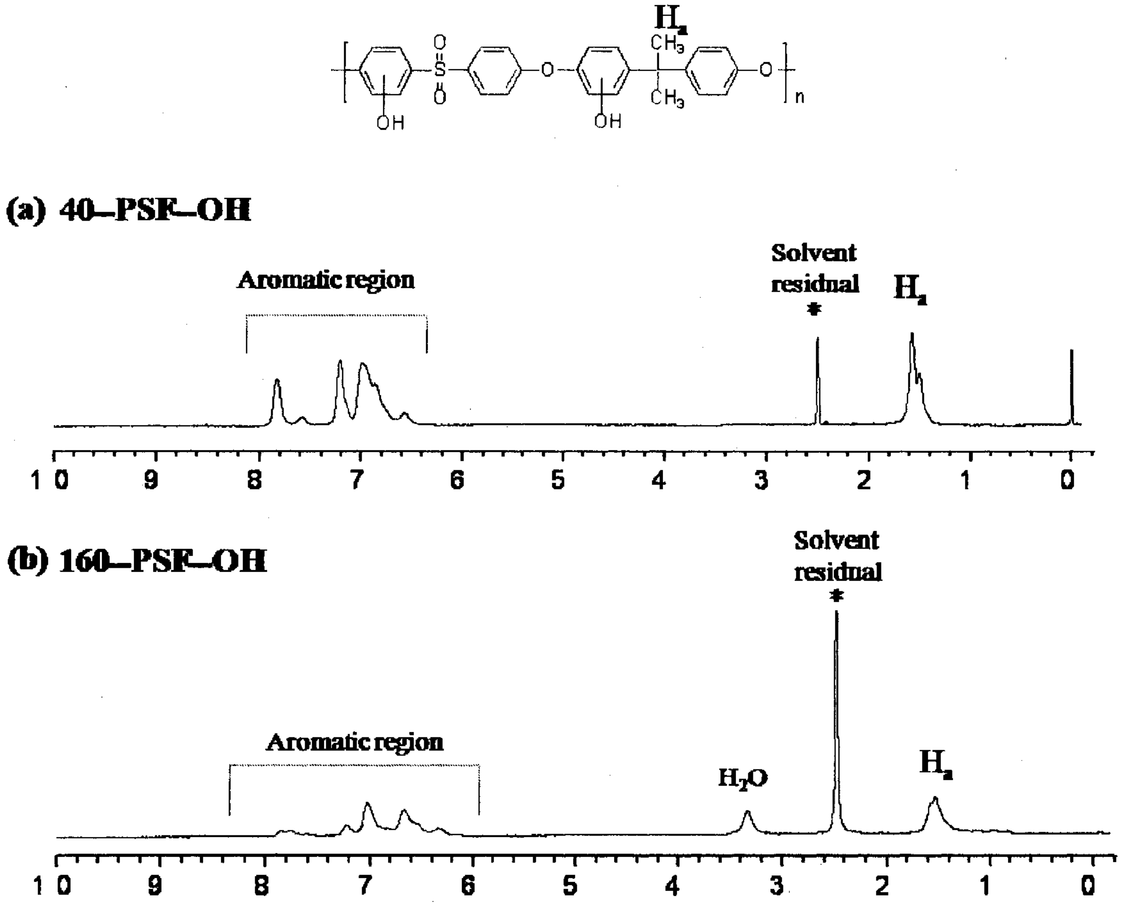


Figure 6. ^{1}H NMR spectra [delay time = 1 s, number of transients = 16] of (a) 40–PSF–OH and (b) 160–PSF–OH [10 mg/mol in DMSO-d_6 at 25°C].

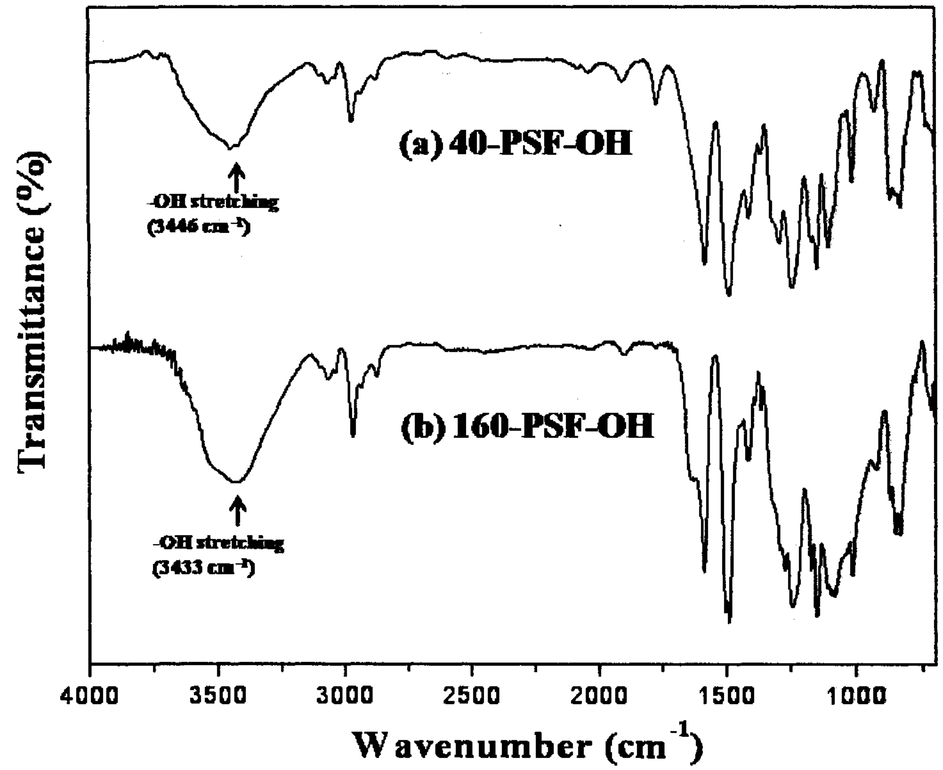
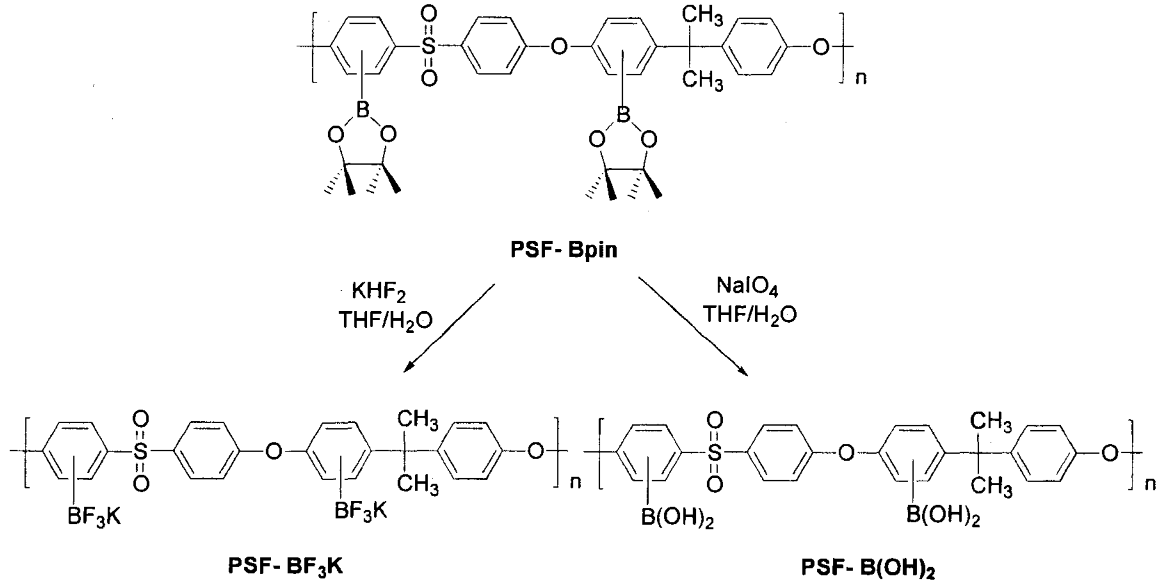


Figure 7. FT-IR spectra of (a) 40–PSF–OH and (b) 160–PSF–OH.

2.3. Synthesis of other boron functionalities ($-B(OH)_2$ and $-BF_3K$) from pinacol boronic ester-functionalized polysulfone

Aryl potassium trifluoroborate ($Ar-BF_3K$) and aryl boronic acid ($Ar-B(OH)_2$) are important boron functionalities that have been commonly used in Suzuki-Miyaura coupling reaction. They have been known for inducing higher reactivity than aryl pinacol boronic ester in Suzuki-Miyaura coupling reaction.[35] Thus, the aryl pinacol boronic ester group of PSF-Bpin was converted to the corresponding aryl potassium trifluoroborate and aryl boronic acid using a literature method (Scheme 19). These new boron functionalities reactions not only serve as a versatile intermediate for further transformations but also improve the polarity of the functionalized polysulfone because of more polar character of the functional groups. Boronic acid-functionalized polysulfone (PSF—$B(OH)_2$) and potassium trifluoroborate-functionalized polysulfone (PSF—BF_3K) were obtained by reacting PSF-Bpin with an aqueous THF solution of $NaIO_4$ and KHF_2 , respectively (Scheme 19). Both 40-PSF-Bpin and 160-PSF-Bpin were tested for these conversions, generating 40—PSF—$B(OH)_2$ and 160—PSF—$B(OH)_2$) from the hydrolysis reaction and 40—PSF—BF_3K and 160—PSF—BF_3K from the fluorination reaction.



Scheme 19. Transformations of pinacol boronic ester-functionalized polysulfone (PSF—Bpin) to boronic acid-functionalized polysulfone (PSF—$B(OH)_2$) and potassium trifluoroborate-functionalized polysulfone (PSF—BF_3K).

Once the aryl Bpin group was hydrolyzed to the aryl boronic acid group, PSF—$B(OH)_2$ was not soluble in chloroform and THF, but exhibited a limited solubility in DMSO. The ^1H NMR spectra of 40–PSF–$B(OH)_2$ and 160–PSF–$B(OH)_2$) obtained from DMSO-d_6 solution showed the resonances of the isopropylidene group and aromatic protons of the polymer main-chain but the methyl resonances of the Bpin group at 1.0~1.3 ppm completely disappeared (Figure 8a–b).

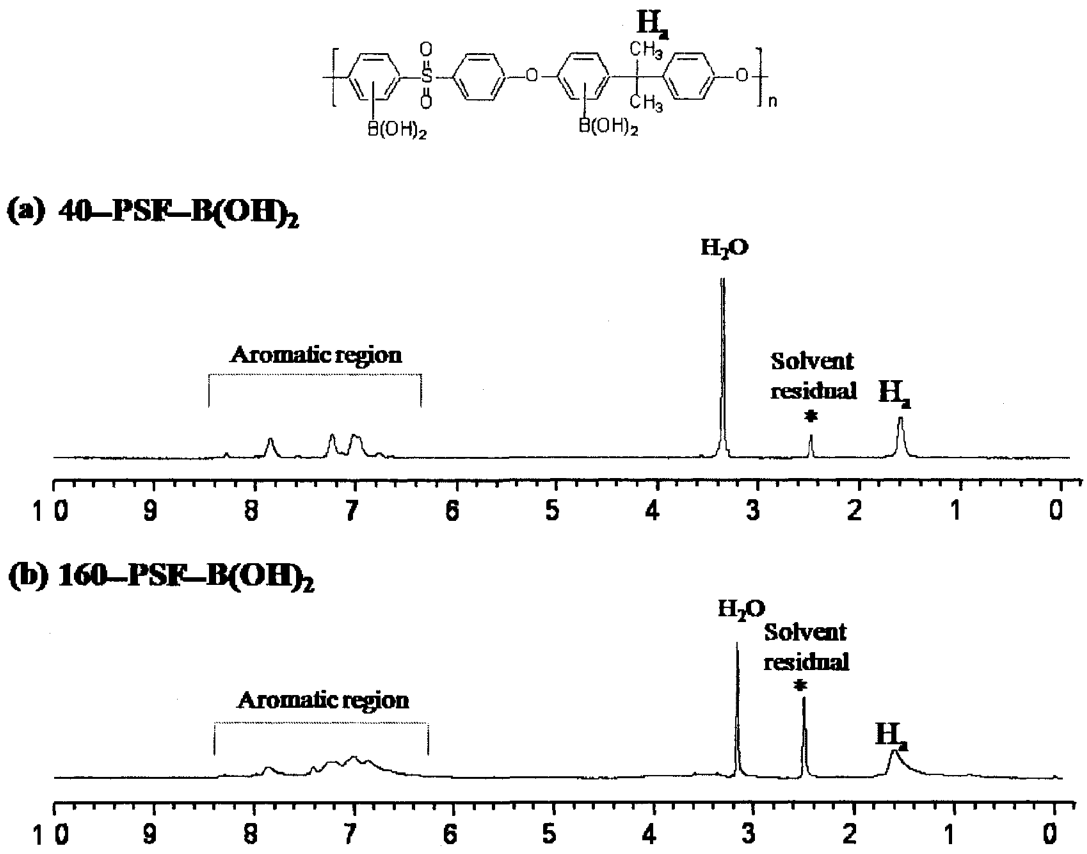


Figure 8. ^1H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–$B(OH)_2$ and (b) 160–PSF–$B(OH)_2$ [10 mg/mL in DMSO-d_6 at 25°C].

^{11}B NMR spectra of PSF–B(OH)$_2$ showed a broad aryl boronic acid peak at 30 ppm and, similar to the ^{11}B NMR spectra of the corresponding PSF–Bpins (Figure 5), the intensity of the boronic acid peak increased as the concentration of boronic acid group in polymer increased (Figure 9a–b).

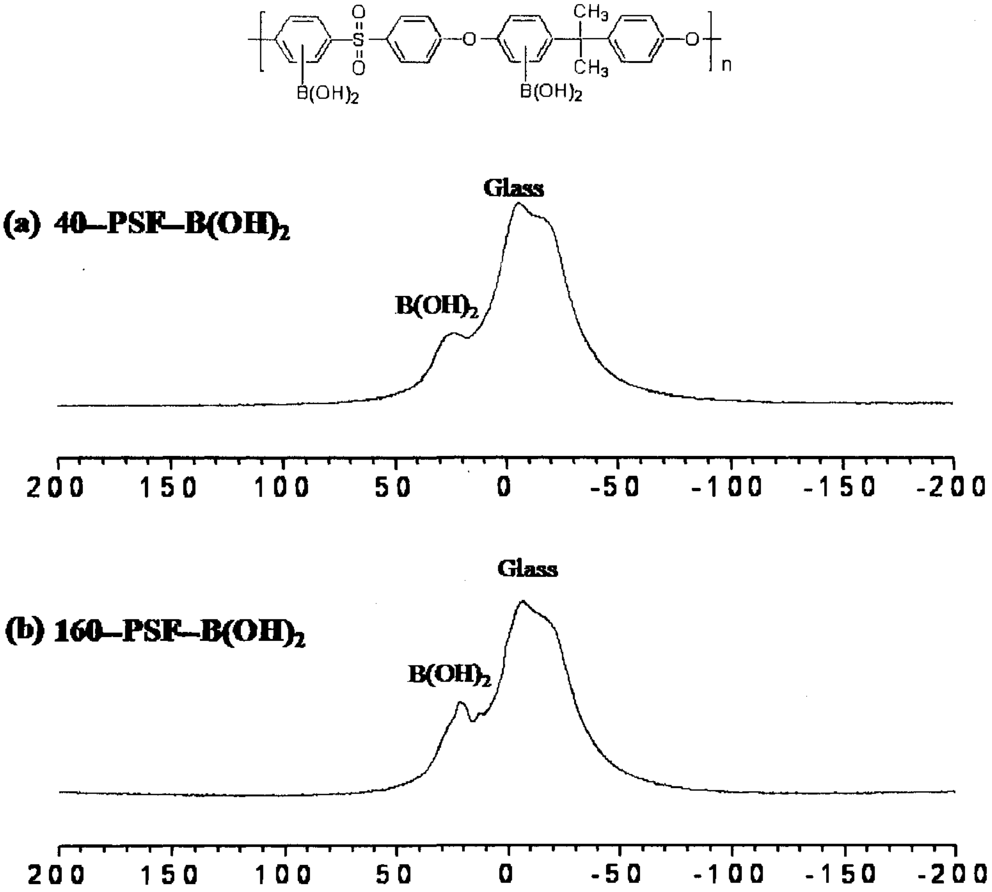


Figure 9. ^{11}B NMR spectra [delay time = 4s, number of transients = 1000] of (a) 40–PSF–B(OH)$_2$ and (b) 160–PSF–B(OH)$_2$ [40 mg/mL in DMSO-d_6 at 25°C].

FT-IR spectra also gave information on the transformation reactions from Bpin to B(OH)$_2$. A strong and broad O—H stretching band from the boronic acid group was shown at 3503cm^{-1} and 3479cm^{-1} in the IR spectra of 40—PSF—B(OH)$_2$ and 160—PSF—B(OH)$_2$, respectively [Figure 10 (a) and (b)]. ^{1}H NMR, ^{11}B NMR, and FT-IR spectra of both 40—PSF—B(OH)$_2$ and 160—PSF—B(OH)$_2$ implied that all Bpin groups were converted to boronic acid groups in both low and high concentration of Bpin attached to polymers.

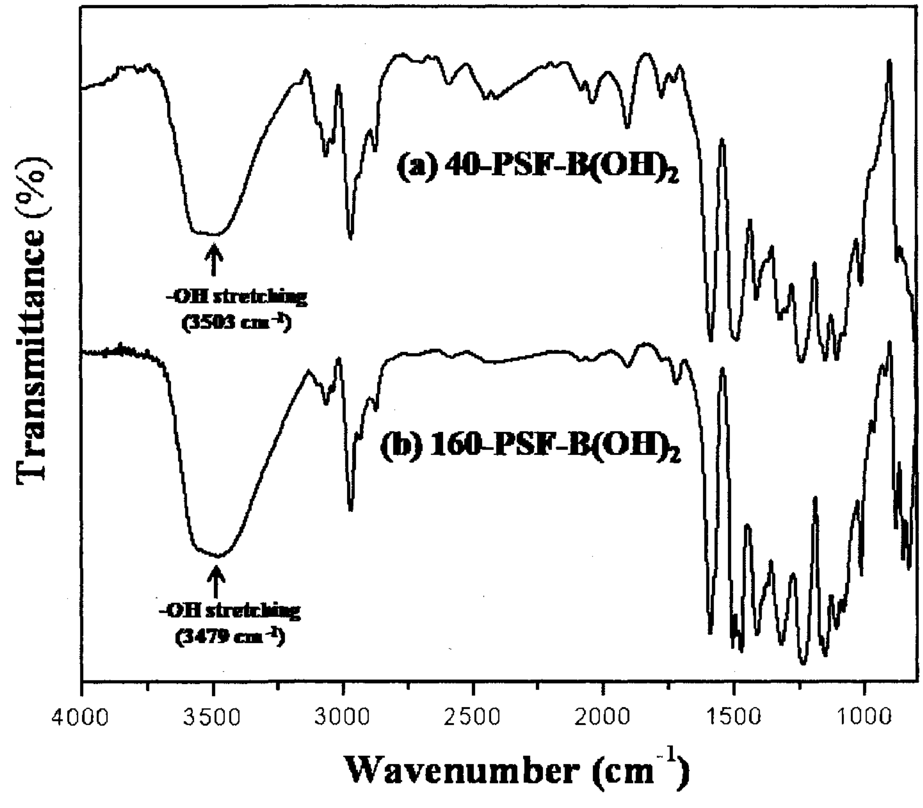


Figure 10. FT-IR spectra of (a) 40—PSF—B(OH)$_2$ and (b) 160—PSF—B(OH)$_2$.

Potassium trifluoroboronate-functionalized polysulfones (40–PSF–BF$_3$K and 160–PSF–BF$_3$K) were prepared from the corresponding PSF-Bpins (40–PSF–Bpin and 160–PSF–Bpin). Similar to the ^{1}H NMR spectrum of PSF-B(OH)$_2$, the ^{1}H NMR spectra of potassium trifluoroboronate-functionalized polysulfones showed resonances of the isopropylidene group and aromatic protons but no resonance resulting from the Bpin group was detected, indicating complete conversion to the potassium trifluoroboronate functionality (Figure 11a–b).

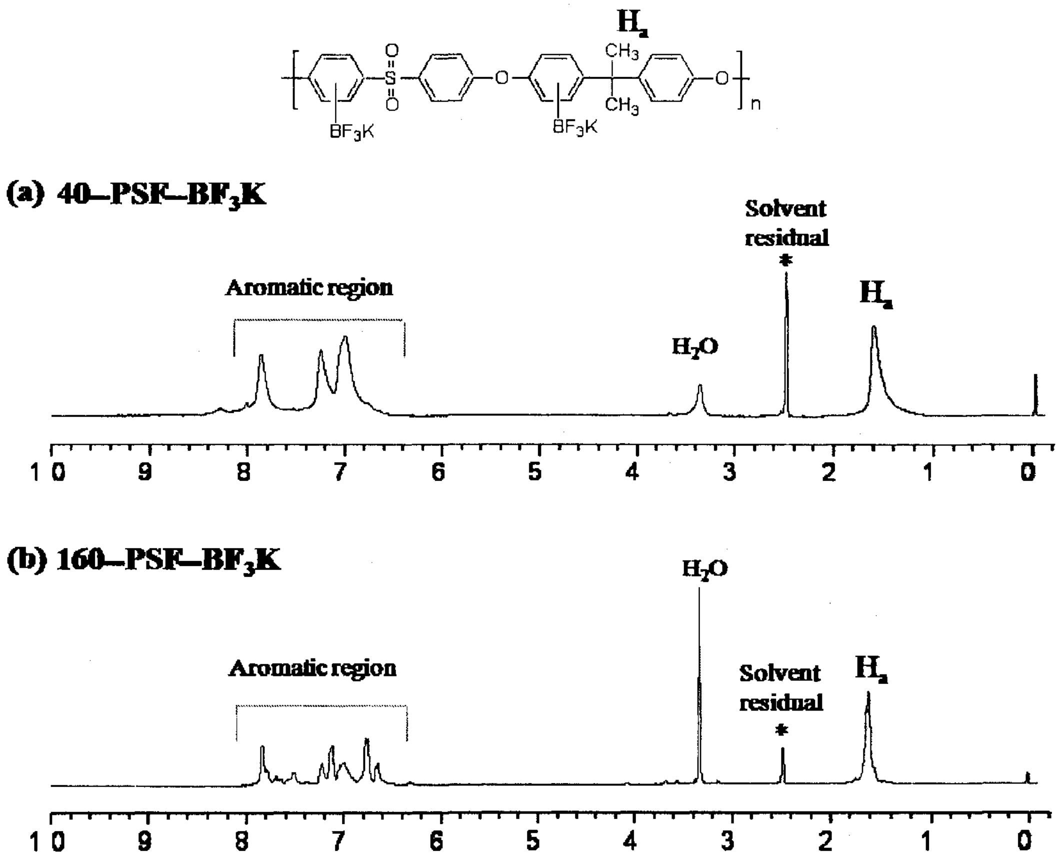
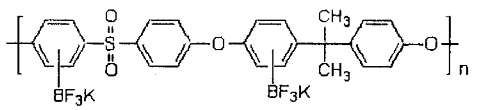
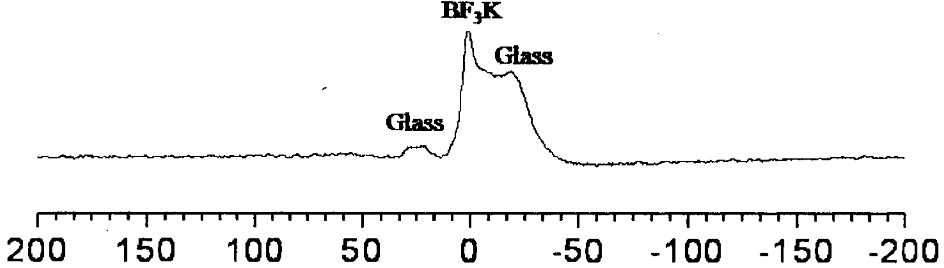


Figure 11. ^{1}H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–BF$_3$K and (b) 160–PSF–BF$_3$K [10 mg/mL in DMSO-d$_6$ at 25°C].

^{11}B NMR spectra of PSF–BF_3K showed an aryl trifluoroborate peak at 1.7 ppm that was relatively sharp than peaks from both pinacol boronic ester and boronic acid, and the intensity of the trifluoroborate peak increased as the concentration of trifluoroborate group in polymer increased (Figure 12a–b).



(a) 40–PSF–BF_3K



(b) 160–PSF–BF_3K

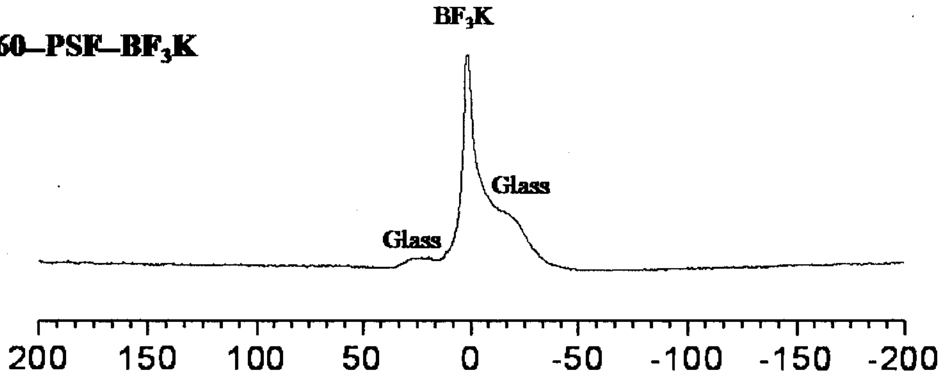


Figure 12. ^{11}B NMR spectra [delay time = 2s, number of transients = 5000] of (a) 40–PSF–BF_3K and (b) 160–PSF–BF_3K [30 mg/mL in DMSO-d_6 at 25°C].

As mentioned earlier, the iridium-catalyzed C–H borylation of polysulfone is expected to result in a mixture of borylated regioisomers. Although identification of each isomer from a mixture of PSF-Bpin is difficult, slightly different ^{1}H NMR chemical shifts corresponding to the Bpin group of different isomers have been observed in the ^{1}H NMR spectra of PSF-Bpins (two different ^{1}H NMR resonances for 40-PSF-Bpin and three different ^{1}H NMR resonances for 160-PSF-Bpin, see Figure 3a–b). The difference in resonances of the regioisomers was also observed in ^{19}F NMR spectra of 40—PSF—BF_3K and 160—PSF—BF_3K (Figure 13a–b). The BF_3K groups located at different sites of the aromatic rings of polysulfone showed slight different ^{19}F NMR resonances. The ^{19}F NMR spectra of 40—PSF—BF_3K showed two resonances of the BF_3K group at –137.2 and –138.5 ppm presumably due to the presence of two regioisomers (Figure 13a). The integral ratio of the two ^{19}F NMR resonances was 17:83. 160—PSF—BF_3K showed four ^{19}F NMR resonances of the BF_3K group at –136.5, –137.2, and –138.4 ppm and the two peaks at –137.2 and –138.5 ppm were more pronounced (Figure 13b). It is believed that the presence of additional ^{19}F NMR resonances in 160—PSF—BF_3K is a result of creation of more regioisomers when the more B_2pin_2 was added during the C–H borylation process.

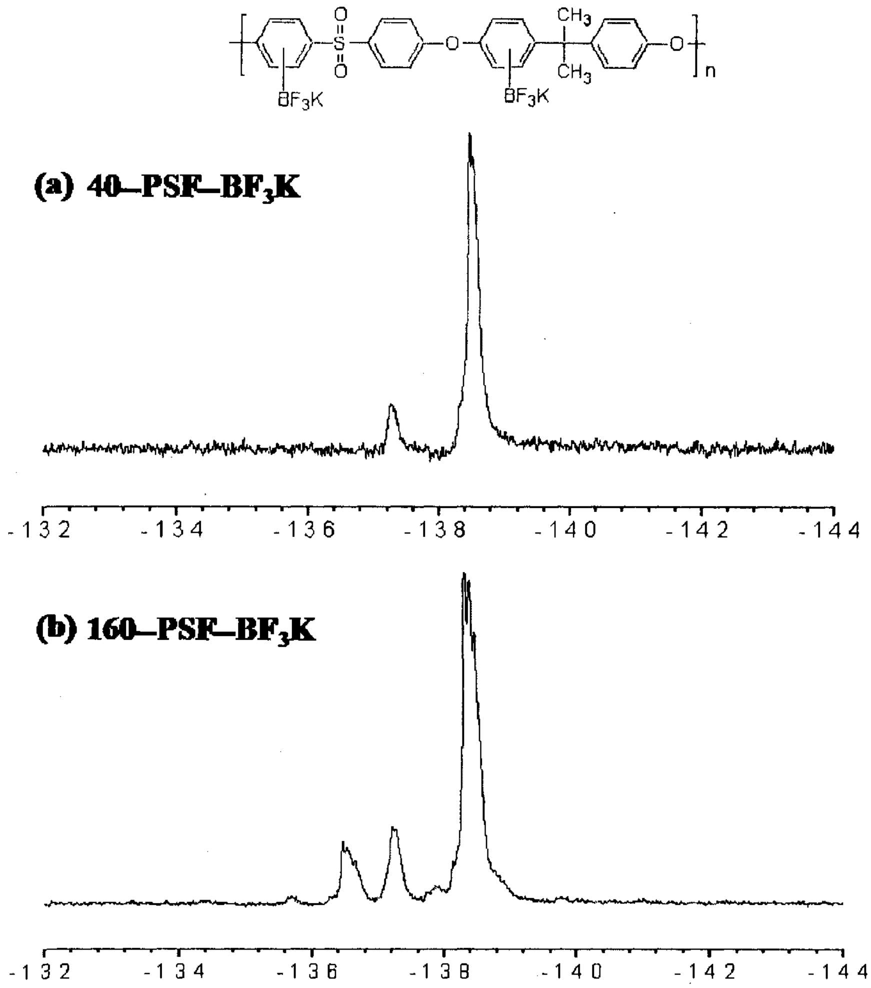
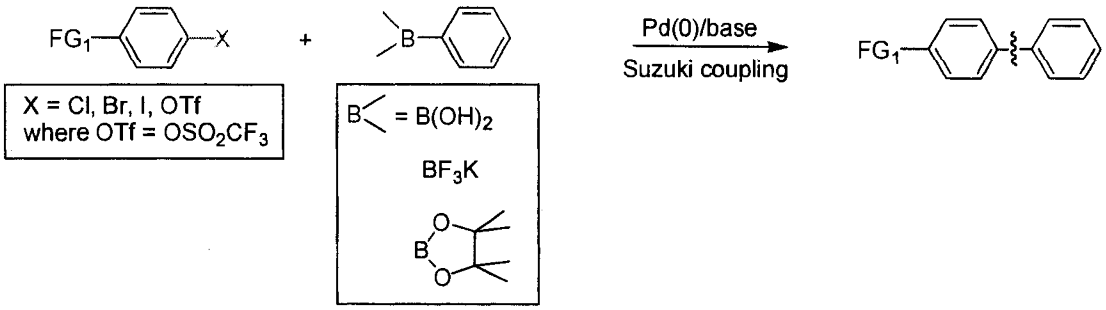


Figure 13. ^{19}F NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–BF_3K and (b) 160–PSF–BF_3K [10 mg/mL in DMSO-d_6 at 25°C].

2.4. Suzuki-Miyaura coupling reaction of Bpin-functionalized polysulfone

Transition metal catalyzed organic reactions have undergone explosive development during the past decade. Among them, the palladium-catalyzed cross-coupling reaction of aryl halide (including pseudo-halides such as triflate) with arylboron compound (e.g., boronic acid and boronic ester) is one of the most popular reactions (Suzuki-Miyaura coupling reaction; Scheme 20).[29, 36] Suzuki-Miyaura coupling is a very powerful synthetic method for the formation of biaryl C–C bond because of its compatibility with a wide range of functional groups and high reactivity even with less than 1 mol% of palladium catalyst.[37, 38, 39, 40] Currently, the Suzuki-Miyaura coupling is widely used to synthesize complex organic molecules and conjugated polymers.[41] Among aryl halides, the reactivity order follows I > Br ≅ OTf >> Cl.



Scheme 20. Suzuki-Miyaura coupling reaction of aryl halide and pseudo halide.

Having established a mild post-functionalization of polysulfone with pinacol boronic ester, we subsequently used the Bpin-functionalized polysulfone (PSF—Bpin) for a potential precursor of various functional group-functionalized polysulfone via Suzuki-Miyaura coupling reaction with aryl bromide. As first test, *p*-bromoacetophenone was allowed to react with PSF—Bpin of various Bpin concentrations under a condition that consists of 3 mol% of $Pd(OAc)_2$, 3 mol% of X-phos (2-dicyclohexylphosphino-2',4',6'-tri-*i*-propyl-1,1'-biphenyl), and K_2CO_3, and a 1:10 mixture of H_2O and THF to give the corresponding acetophenone-functionalized polysulfones (PSF—Ar—$COCH_3$, see Scheme 21a). The results of Suzuki-Miyaura coupling reaction with *p*-bromoacetophenone are summarized in Table 2 and it clearly demonstrates that the Bpin functional group of PSF-Bpin was completely converted to acetophenone group functionality with a similar concentration.

Table 2. Suzuki-Miyaura coupling reaction of PSF—Bpin to synthesize acetophenone functionalized polysulfone (PSF—Ar—$COCH_3$).

entry	PSF—Bpin		PSF—Ar—$COCH_3$[a]
	$[B_2pin_2]/[PSF]$[b]	Bpin (mol %)[c]	$COCH_3$ (mol %)[d]
1	0.2	0	0
2	0.4	41	38
3	0.6	56	57
4	0.8	66	67
5	1.0	86	87
6	1.2	108	101
7	1.4	128	133
8	1.6	148	146
9	1.8	179	172
10	2.0	186	175

[a] Suzuki-Miyaura coupling reactions were conducted with 98 mg of of PSF—Bpin in the presence of 3 mol% of $Pd(OAc)_2$ and 3 mol% of X-phos ligand relative to the amount of Bpin that is attached to polymer in 1 mL of THF at 80°C for 6h.

[b] Molar ratio of B_2pin_2 added relative to the repeating unit of polymer in the C–H borylation process.

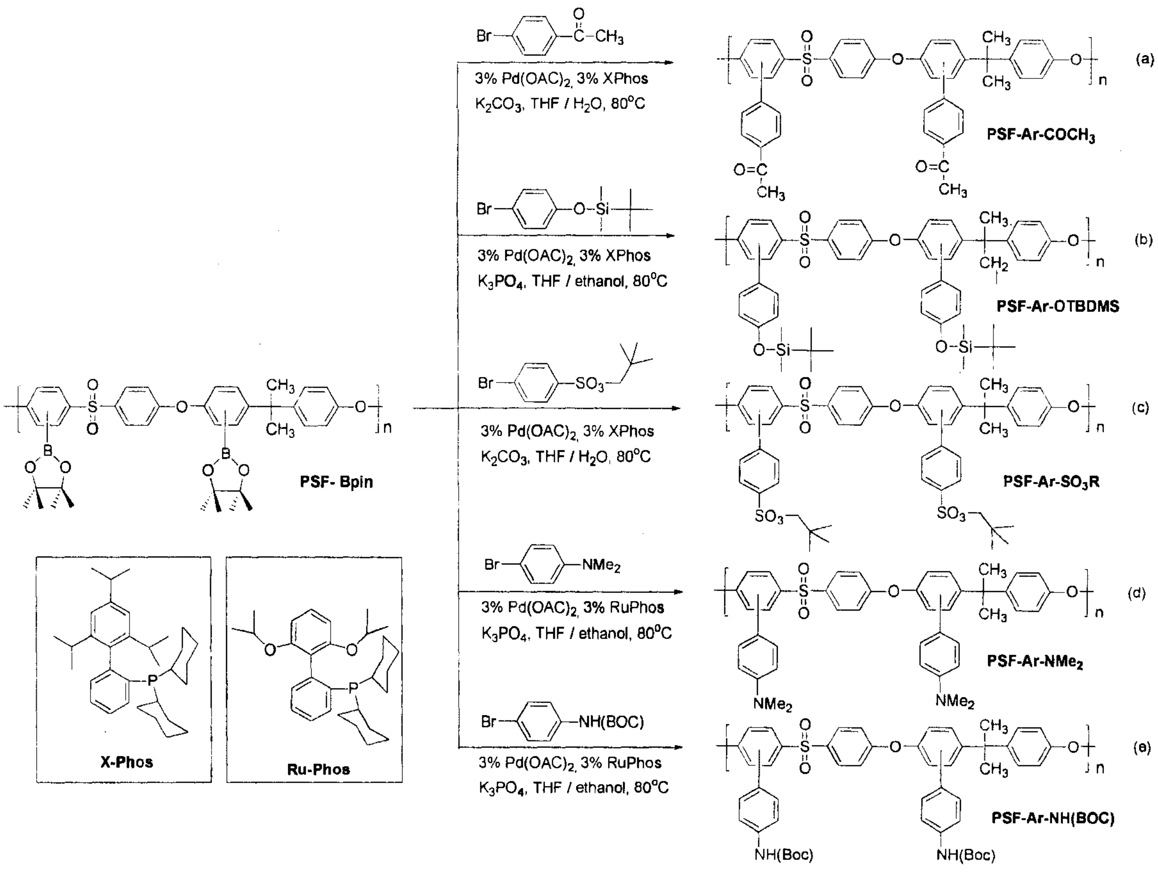
[c] Mol% of Bpin-functionalized polysulfone repeating unit. Calculated from the ^1H NMR spectrum of PSF-Bpin.

[d] Mol% of acetophenone-functionalized polysulfone repeating unit. Calculated from the ^1H NMR spectrum by integral ratio of the two methyl groups of isopropylidene group in polysulfone main-chain and the methyl group of acetophenone group attached to polymer.

In addition to the results of PSF—Ar—$COCH_3$, a variety of polar functional groups installed to polysulfone via a similar Suzuki-Miyaura coupling reactions of PSF—Bpin: 4-bromophenoxy-*tert*-butyldimethylsilane, neopentyl 4-bromophenylsulfonate ester, 4-bromo-N,N'-dimethylaniline, and 4-bromo-N-*tert*-butoxycarbonyl aniline were coupled with PSF—Bpin to produce the aryl *tert*-butyldimethylsilane-functionalized polysulfone (PSF—Ar—OTBDMS), neopentyl aryl sulfonate-functionalized polysulfone

(PSF–Ar–SO_3R), N,N'-dimethylaniline-functionalized polysulfone (PSF–Ar–NMe_2), and N-*tert*-butoxycarbonyl aniline-functionalized polysulfone (PSF–Ar–NH(Boc)), respectively (Scheme 21b–e). By changing functional group in the para position of aryl bromide, a variety of polar functional groups, such as ketone, sulfonic ester, silane, 3^o amine, and protected 1^o amine, could be incorporated to polysulfone from a common polymer precursor.

Particularly notable examples of the Suzuki-coupled polymer products are PSF–Ar–SO_3R and PSF–Ar–NH(Boc), because these protected functional groups in the polymers can be converted to arylsulfonic acid (–ArSO_3H) and 1^o aryl amine (–ArNH_2) by simple deprotection reactions. For detailed studies of the Suzuki-Miyaura coupling reaction, two borylated polymer products that were generated two different ratios of B_2pin_2 relative to the polymer repeating unit (i.e., 40–PSF–Bpin and 160–PSF–Bpin) were selected to represent low and high concentrations of Bpin groups in the polysulfone. Using the Suzuki-Miyaura coupling reaction, 40–PSF–Bpin and 160–PSF–Bpin were converted to corresponding Suzuki-Miyaura coupling products while maintaining the same level of concentration of the functional group (see Table 3). This result demonstrates that the Bpin group of PSF-Bpin serves as a versatile intermediate via Suzuki-Miyaura coupling reactions for creation of various functionalities in the polymer.



Scheme 21. Installation of various functionalities into polysulfone (PSF-Ar) via Suzuki-Miyaura coupling reactions of PSF–Bpin.

Table 3. Suzuki-Miyaura coupling reactions of PSF—Bpin to synthesize various functionalized polysulfones (PSF-Ar).

	PSF—Bpin		PSF—Ar[a]				
			PSF—Ar —$COCH_3$	PSF—Ar —OTBDMS	PSF—Ar —SO_3R	PSF—Ar —NMe_2	PSF—Ar —NH(Boc)
entry	[B_2pin_2]/ [PSF][b]	Bpin (mol %)[c]	$COCH_3$ (mol %)[c]	OTBDMS (mol %)[c]	SO_3R (mol %)[c]	NMe_2 (mol %)[c]	NH(Boc) (mol %)[c]
1	0.4	41	38	36	38	37	42
2	1.6	148	146	125	110	145	148

[a] Suzuki-Miyaura coupling reactions were conducted with 98 mg of of PSF—Bpin in the presence of 3 mol% of $Pd(OAc)_2$ and 3 mol% of X-phos ligand relative to the amount of Bpin that is attached to polymer in 1 mL of THF at 80°C for 6 h.

[b] Molar ratio of B_2pin_2 added relative to the repeating unit of polymer in the C–H borylation process.

[c] Mol% of functional group in polysulfone repeating unit. Calculated from ^1H NMR spectrum.

2.4.1. Acetophenone-functionalized polysulfone (PSF–Ar–$COCH_3$)

A condition composed of 3 mol% of $Pd(OAc)_2$, 3 mol% of X-Phos, K_2CO_3 , and a 1:10 mixture of H_2O and THF was employed to couple *p* -bromoacetophenone with 40—PSF—Bpin and 160—PSF—Bpin and to produce the corresponding polymer products, 40—PSF—Ar—$COCH_3$ and 160—PSF—Ar—$COCH_3$ (Scheme 21a). The ^1H NMR spectra of 40—PSF—Ar—$COCH_3$ and 160—PSF—Ar—$COCH_3$ showed a complete disappearance of the methyl resonance of the Bpin group and new appearance of resonance at 2.6 ppm from the methyl group of the acetophenone with the same concentrations of the Bpin concentration of the starting polymer. As the concentration of acetophenone increased from 40—PSF—Ar—$COCH_3$ and 160—PSF—Ar—$COCH_3$, the intensity of the resonance at 2.6 ppm from the acetophenone group (H_b of Figure 14a–b) was accordingly augmented.

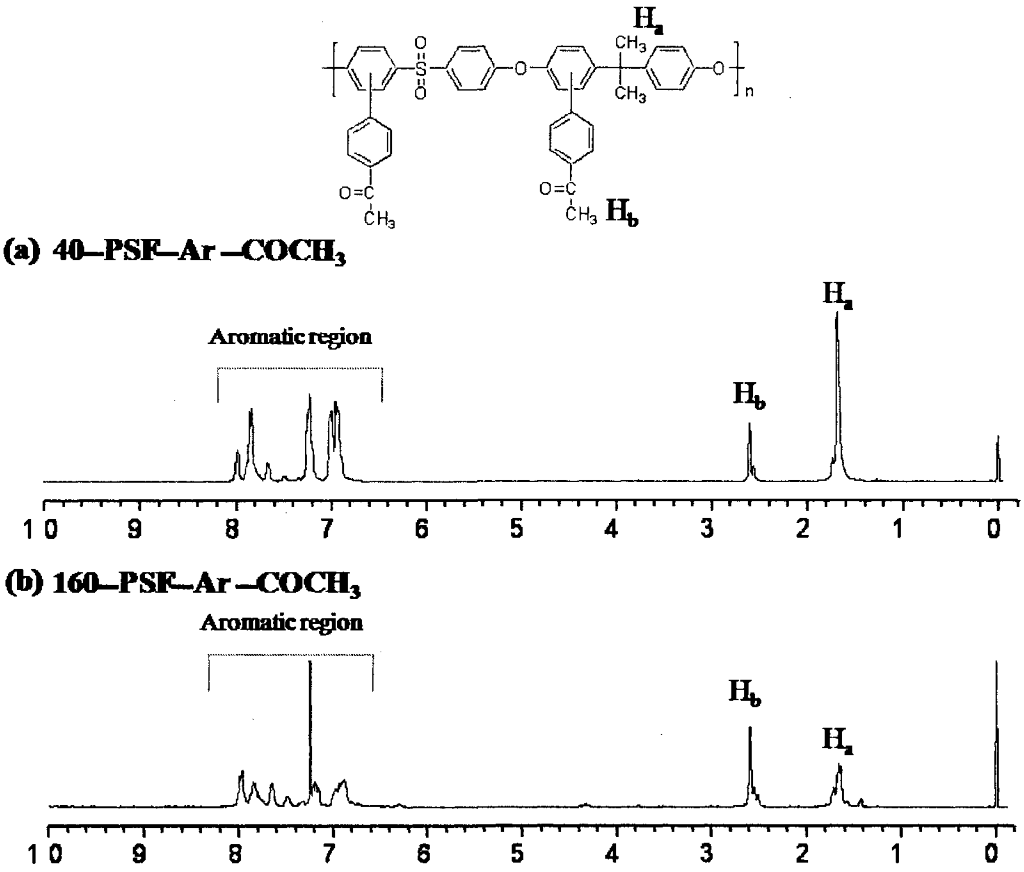


Figure 14. ^{1}H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–Ar–COCH$_3$ and (b) 160–PSF–Ar–COCH$_3$ [10 mg/mL in CDCl$_3$ at 25°C].

Conjugation between C=O bond and aromatic C=C bond of aromatic ring is known to reduce absorption frequency of C=O to the range of 1685–1666 cm^{-1} in IR due to the delocalization of π electrons absorption.[42] In FT-IR spectra of PSF—Ar—$COCH_3$, C=O stretching bands of the ketone group in 40—PSF—Ar—$COCH_3$ and 160—PSF—Ar—$COCH_3$ were observed at 1684 cm^{-1} and 1682 cm^{-1}, respectively (Figure 15a–b).

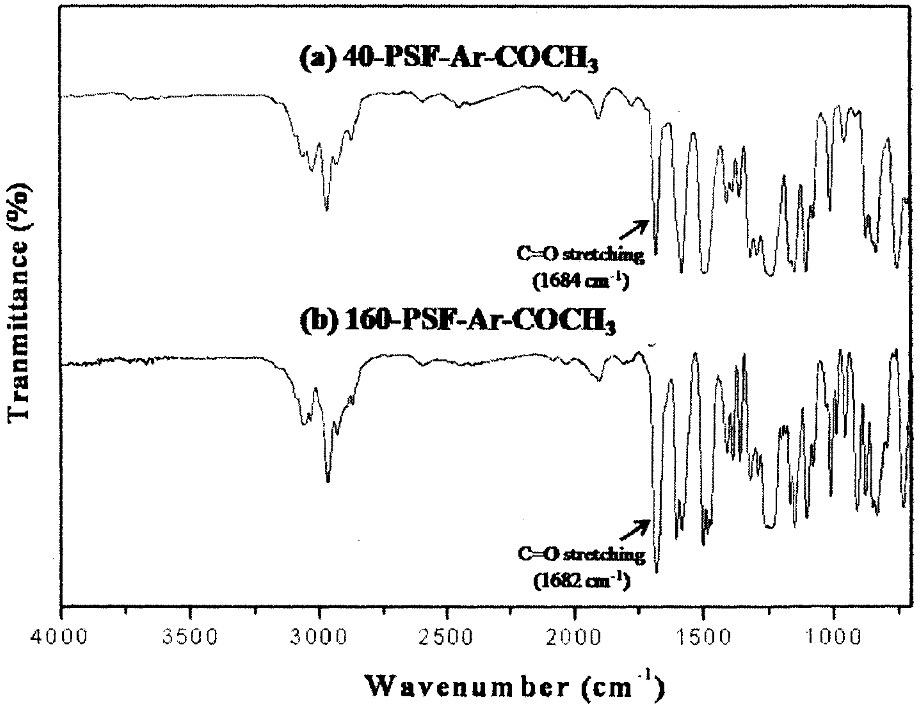
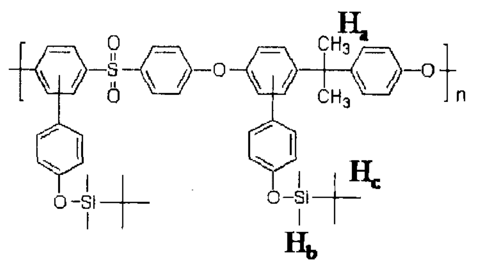


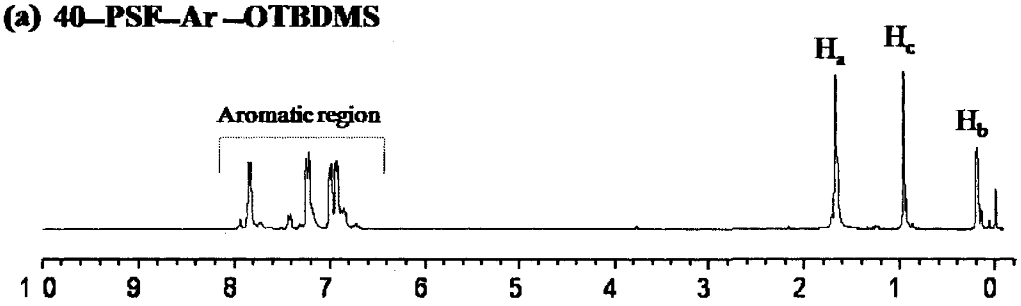
Figure 15. FT-IR spectra of (a) 40—PSF—Ar—$COCH_3$ and (b) 160—PSF—Ar—$COCH_3$.

2.4.2. *tert*-Butyldimethylsiloxyphenyl-functionalized polysulfone (PSF–Ar–OTBDMS)

4-Bromophenoxy-*tert*-butyldimethylsilane was coupled with 40–PSF–Bpin and 160–PSF–Bpin to give the corresponding *tert*-butyldimethylsiloxyphenyl-functionalized polysulfones, 40–PSF–Ar–OTBDMS and 160–PSF–Ar–OTBDMS, respectively. The same condition that had been used for the Suzuki-Miyaura coupling with *p*-bromoacetophenone was employed (3 mol% of $Pd(OAc)_2$, 3 mol% of X-Phos, and K_2CO_3 in a 1:10 mixture of H_2O and THF) for the Suzuki-Miyaura coupling of PSF-Bpin with 4-bromophenoxy-*tert*-butyldimethylsilane (Scheme 21b). The ^1H NMR spectra of both 40–PSF–Ar–OTBDMS and 160–PSF–Ar–OTBDMS showed a complete disappearance of the methyl protons of the Bpin group while the two methyl groups at 0.20 ppm and the *tert*-butyl group at 0.98 ppm from the *tert*-butyldimethylsilane group appeared with a similar concentration of Bpin in the starting polymer (Figure 16a–b). As the concentration of *tert*-butyldimethylsiloxy (OTBDMS) group increased in the polymers, the intensity of the resonances of the OTBDMS group (H_b and H_c of Figure 16a–b) increased.



(a) 40–PSF–Ar–OTBDMS



(b) 160–PSF–Ar–OTBDMS

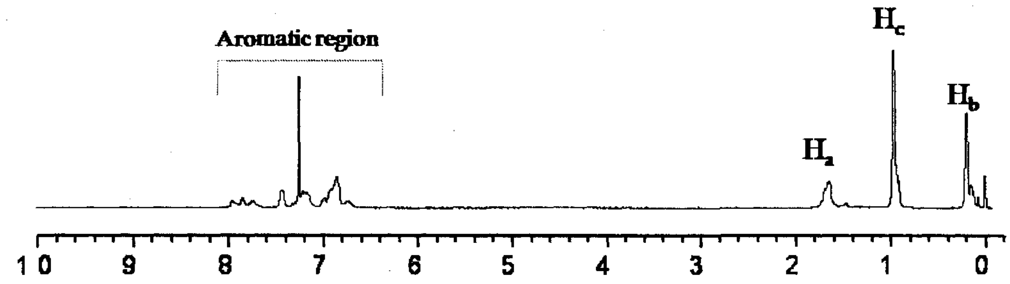


Figure 16. ${}^{1}H$ NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–Ar–OTBDMS and (b) 160–PSF–Ar–OTBDMS [10 mg/mL in $CDCl_3$ at 25°C].

2.4.3. Neopentyl arylsulfonate ester-functionalized polysulfone

(PSF–Ar–SO_3R)

Neopentyl arylsulfonate ester, a protected form of sulfonic acid, was introduced to polysulfone by Suzuki-Miyaura coupling of 40–PSF–Bpin and 160–PSF–Bpin with neopentyl 4-bromophenylsulfonate ester. The resulting neopentyl arylsulfonate ester-functionalized polysulfones (40–PSF–Ar–SO_3R and 160–PSF–Ar–SO_3R) were obtained the same coupling condition used for PSF-Ar-$COCH_3$, using 3 mol % of

$Pd(OAc)_2$, 3 mol% of X-Phos, and K_2CO_3 in a 1:10 mixture of H_2O and THF (Scheme 21c). In the ^{1}H NMR spectra of 40–PSF–Ar–SO_3R and 160–PSF–Ar–SO_3R, the methyl resonance of the Bpin group was completely removed and two new resonances from the methylene group at 3.7 ppm and the *tert*-butyl group of neopentyl group at 0.9 ppm appeared with a similar concentration of the starting polymer (Figure 17a–b).

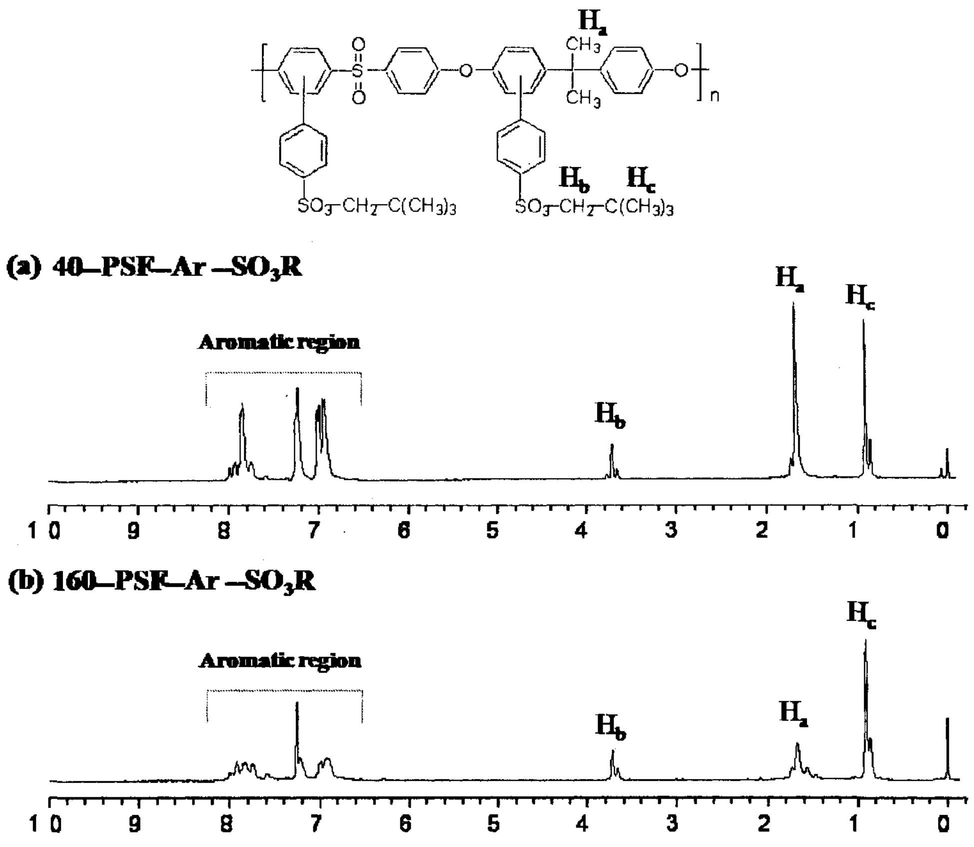


Figure 17. ^{1}H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–Ar–SO_3R and (b) 160–PSF–Ar–SO_3R [10 mg/mL in $CDCl_3$ at 25°C].

S–O stretching in the sulfonate ester appeared at 964 cm^{-1} and at 963 cm^{-1} in the FT-IR spectra of 40–PSF–Ar–SO_3R and 160–PSF–Ar–SO_3R, respectively (Figure 18).

By increasing the concentration of the sulfonate ester in the polymer, the intensity of the S–O stretching also increased.

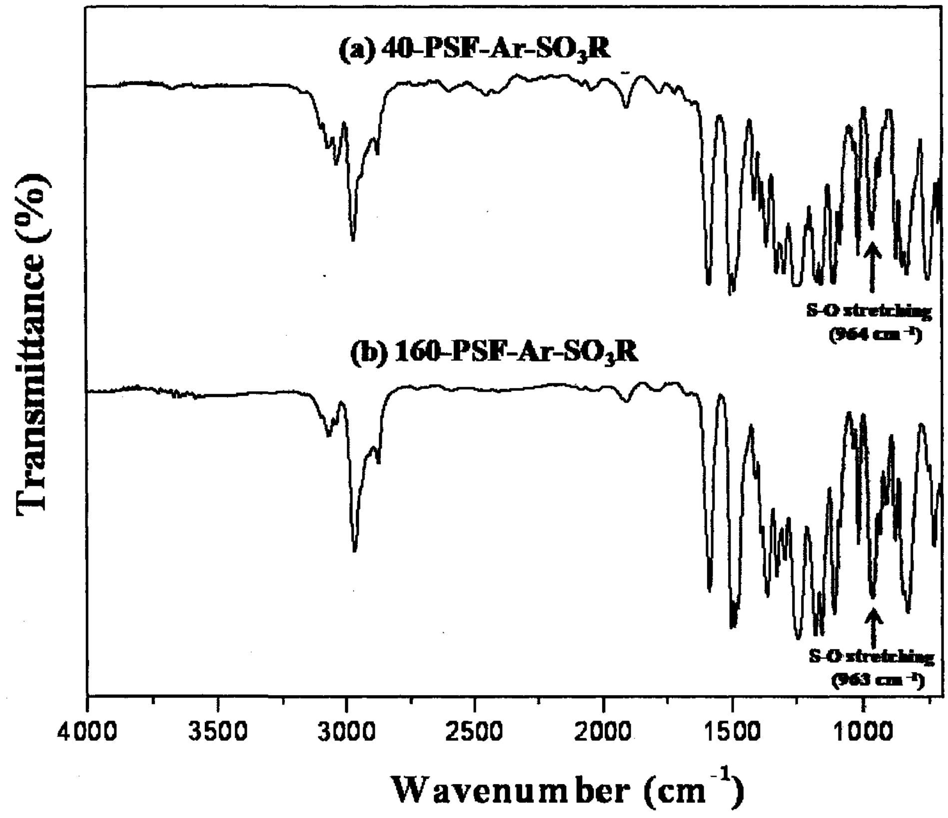
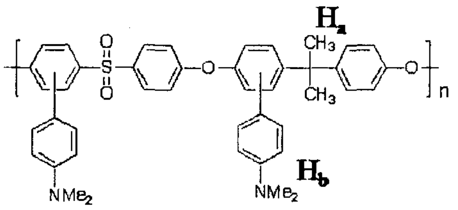


Figure 18. FT-IR spectra of (a) 40–PSF–Ar–SO$_3$R and (b) 160–PSF–Ar–SO$_3$R.

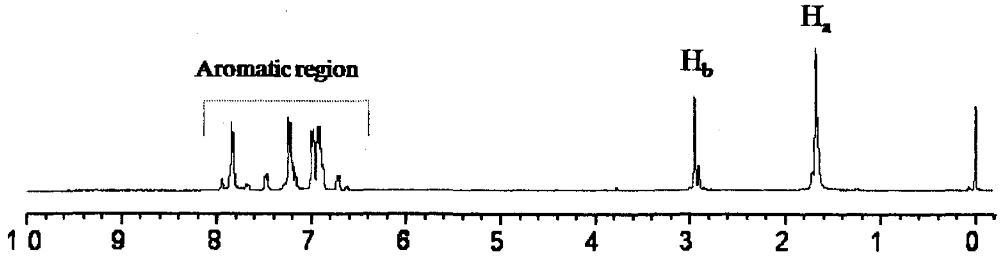
2.4.4. N, N'-Dimethylaniline-functionalized polysulfone (PSF–Ar–NMe$_2$)

We demonstrated that an aromatic tertiary amine could be incorporated into polysulfone via Suzuki-Miyaura coupling reaction of PSF-Bpin with *p*-bromo-N,N'-dimethylaniline. The N, N'-dimethylaniline-functionalized polysulfone (PSF–Ar–NMe$_2$)

was also obtained by a slightly modified coupling condition of PSF-Ar-$COCH_3$: 3 mol% of $Pd(OAc)_2$, 3 mol% of 2-dicyclohexylphosphino-2',6'-di-*i*-propoxy-1,1'-biphenyl (Ru-Phos), and K_3PO_4 in a 1:10 mixture of ethanol and THF (Scheme 21d). The ^1H NMR spectra of 40–PSF–Ar–NMe_2 and 160–PSF–Ar–NMe_2 showed a complete disappearance of methyl resonance of the Bpin group and an appearance of two new methyl groups of N,N'-dimethylaniline at 2.9 ppm with a similar concentration of the starting polymer (Figure 19a–b).



(a) 40–PSF–Ar–NMe_2



(b) 160–PSF–Ar–NMe_2

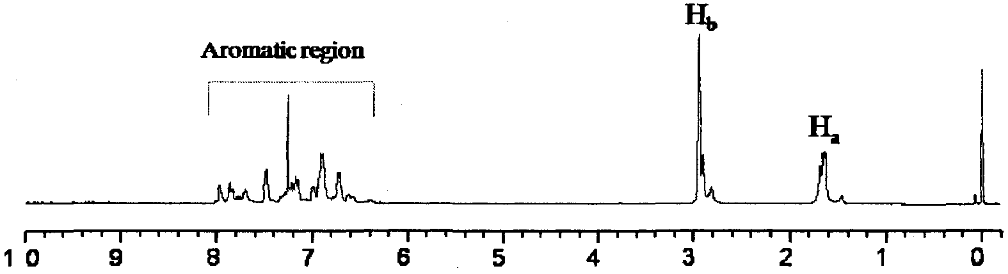
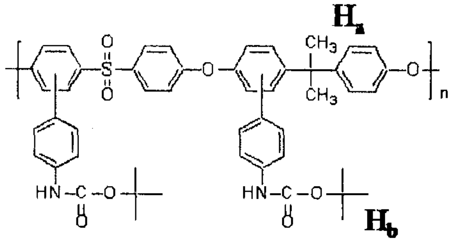


Figure 19. ^1H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–Ar–NMe_2 and (b) 160–PSF–Ar–NMe_2 [10 mg/mL in $CDCl_3$ at 25°C].

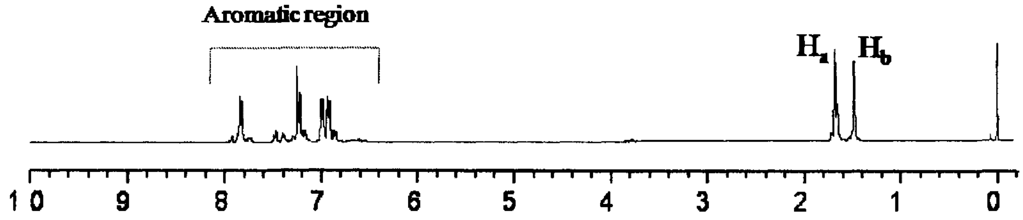
2.4.5. N-*tert*-Butoxycarbonylaniline-functionalized polysulfone (PSF—Ar—NH(BOC)) and its deprotected product, aniline-functionalized polysulfone (PSF—Ar—NH_2)

Using the same coupling condition of PSF—Ar—NMe_2, 4-bromo-N-*tert*-butoxycarbonylaniline (4-Br-C_6H_4-NH(BOC)) was coupled with PSF—Bpin to give PSF—Ar—NH(BOC) (Scheme 21e). The NH(Boc)-functionalized polysulfone is a good precursor of primary amine functionality since *t*-butoxycarbonyl (BOC) group, a common protecting group of amine, would not interfere the Suzuki-Miyaura coupling reaction and could be removed under mild condition to generate –NH_2 group. The ^1H NMR spectra of 40—PSF—Ar—NH(BOC) and 160—PSF—Ar—NH(BOC) showed a complete disappearance of the methyl resonance of the Bpin group and a new resonance of the *t*-butyl group from —NH(BOC) at 1.4 ppm with a similar concentration of the starting polymer (Figure 20a–b).

In the FT-IR spectra of 40—PSF—Ar—NH(BOC) and 160—PSF—Ar—NH(BOC), C=O stretching absorbance appeared at 1729 and 1725 cm^{-1}, respectively (Figure 21a–b). The absorption bands of secondary amide N—H stretching were also observed at 3338 and 3353 cm^{-1}. The absorption bands of N—H bending vibration appeared at 1583 and 1585 cm^{-1} for 40—PSF—Ar—NH(BOC) and 160—PSF—Ar—NH(BOC), respectively.



(a) 40–PSF–Ar–NH(BOC)



(b) 160–PSF–Ar–NH(BOC)

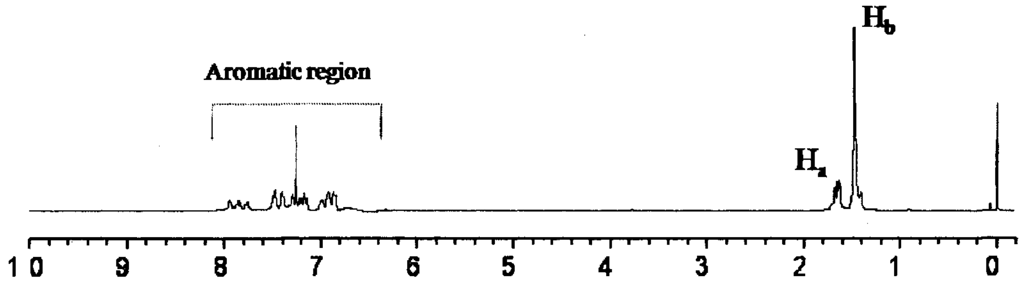


Figure 20. ^{1}H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–Ar–NH(BOC) and (b) 160–PSF–Ar–NH(BOC) [10 mg/mL in $CDCl_3$ at 25°C]

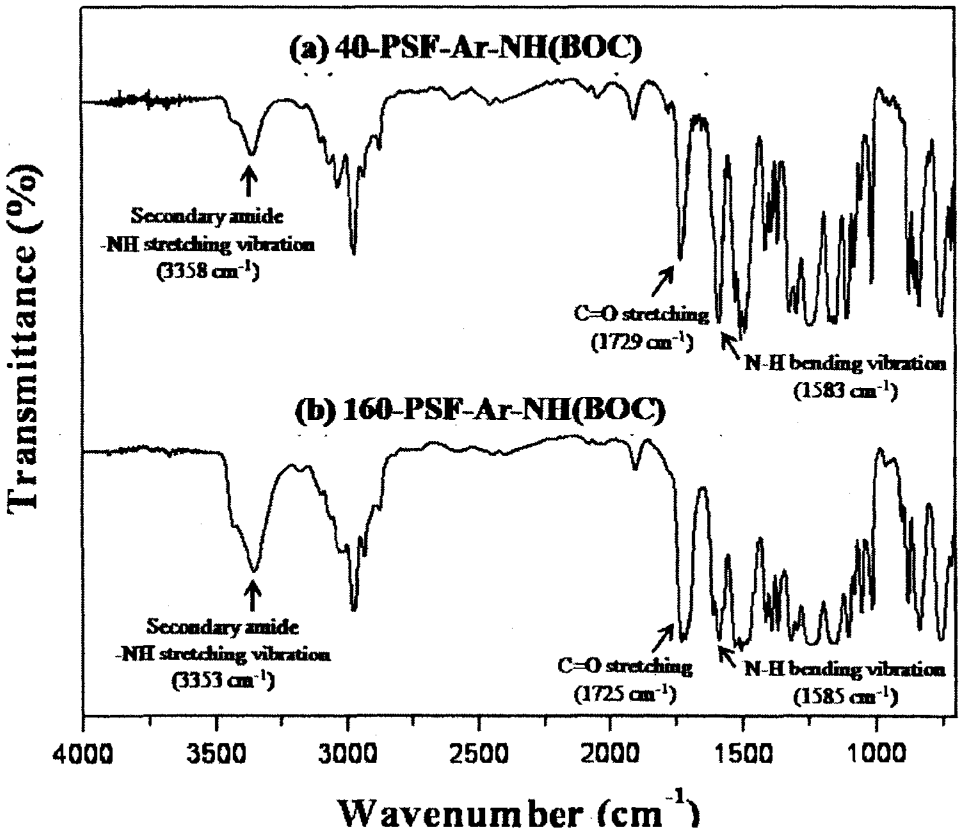
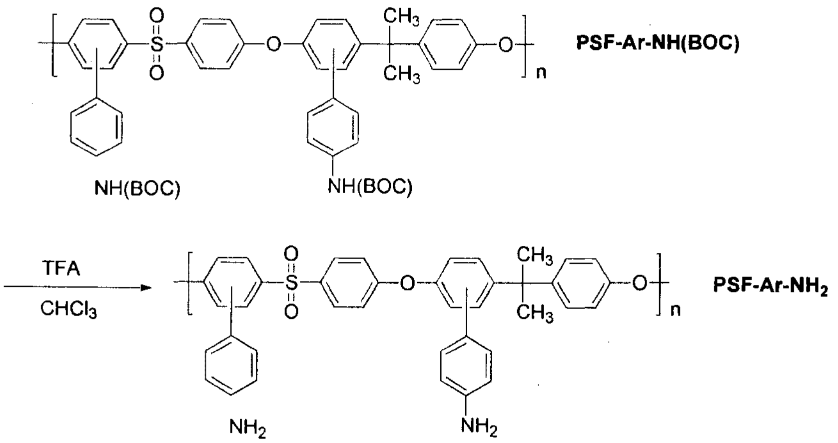


Figure 21. FT-IR spectra of (a) 40–PSF–Ar–NH(BOC) and (b) 160–PSF–Ar–NH(BOC).

The Boc protecting group of PSF–Ar–NH(BOC) was removed with trifluoroacetic acid (TFA) in $CHCl_3$ to generate a primary amine functionality on the polysulfone (Scheme 22). Upon deprotection, the aniline-functionalized polysulfone (PSF–Ar–NH_2) showed a marked solubility difference in common organic solvent because of presence of more polar primary amine group in the polymer. In the ^1H NMR spectrum of 40–PSF–Ar–NH_2, the resonance of the *t*-butyl group of the Boc disappeared, indicating complete removal of the protecting group (Figure 22). Unfortunately, the ^1H NMR spectrum of 160–PSF–Ar–NH_2 could not be obtained because the polymer containing higher concentration of primary amine functionality was not soluble in any deutrated solvents after the deprotection process.



Scheme 22. Deprotection reaction of BOC group to synthesize aniline-functionalized polysulfone (PSF–Ar–NH$_2$).

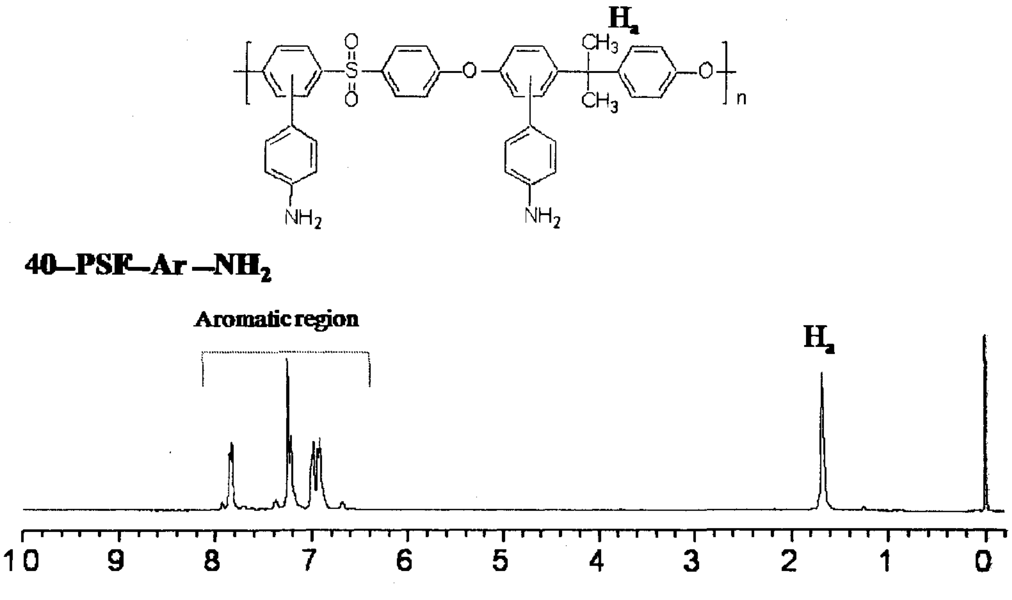


Figure 22. ^{1}H NMR spectrum [delay time = 1s, number of transients = 16] of 40–PSF–Ar–NH$_2$ [10 mg/mL in CDCl$_3$ at 25°C].

The FT-IR spectrum of 40—PSF—Ar—NH_2 showed disappearance of the C=O stretching band at 1750 cm^{-1} and appearance of two new absorption bands from the primary amine at 3479 cm^{-1} and 3383 cm^{-1} (Figure 23a). Similarly in the FT-IR spectrum of 160—PSF—Ar—NH_2, the C=O stretching band at 1750 cm^{-1} disappeared and two new absorption bands from the primary amine appeared at 3451 cm^{-1} and 3380 cm^{-1} with higher intensity than that of 40—PSF—Ar—NH_2 (Figure 23b).

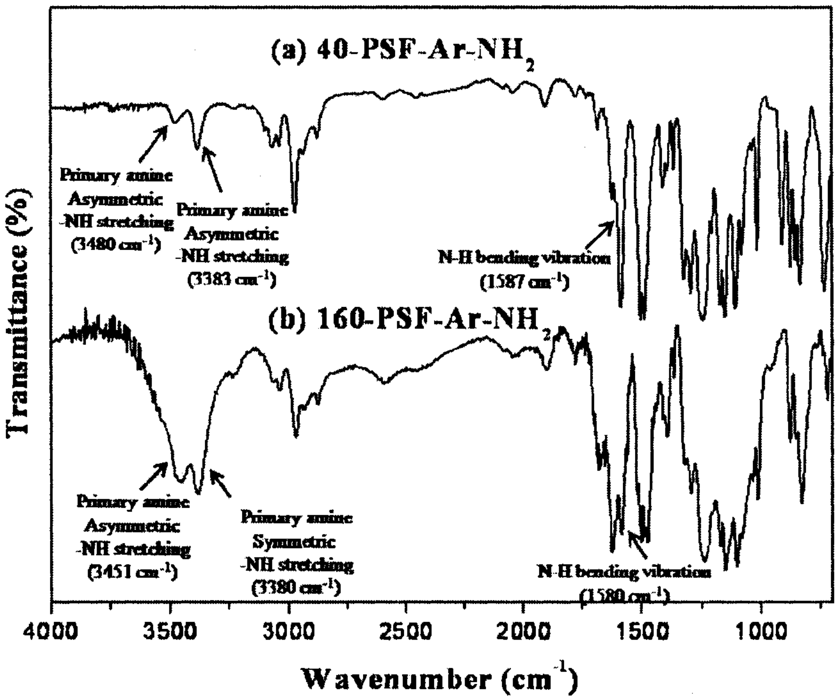
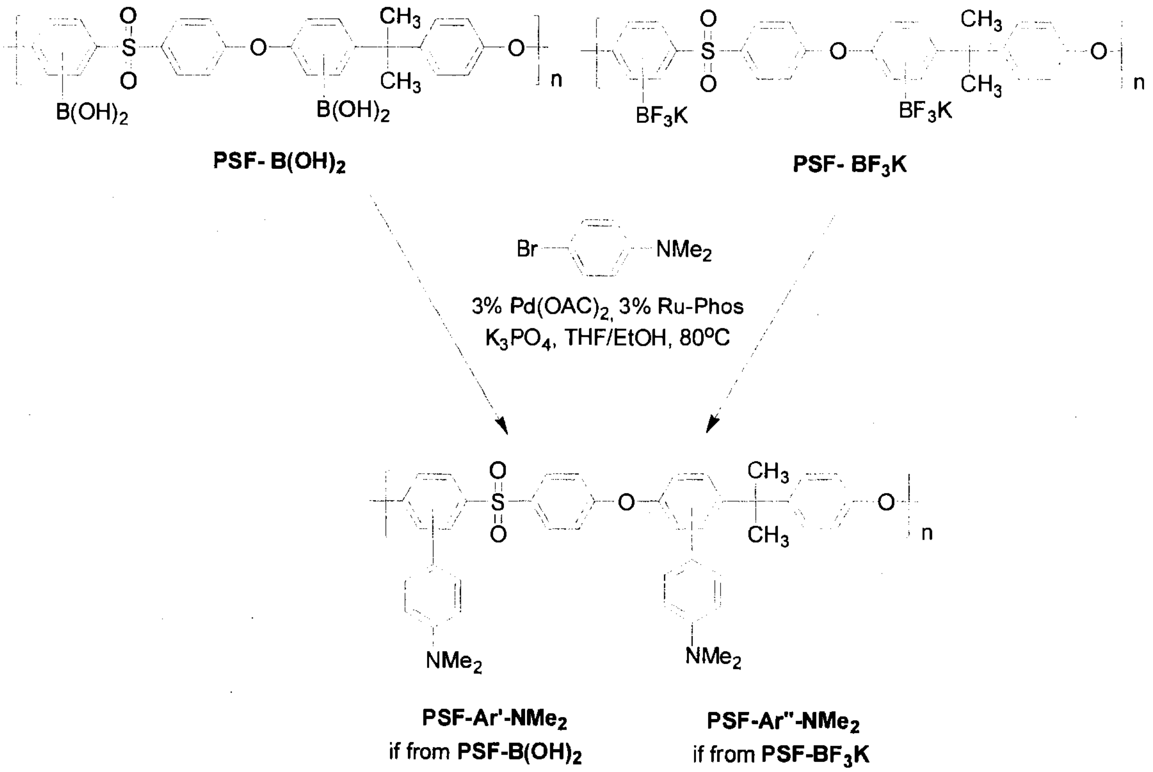


Figure 23. FT-IR spectra of (a) 40—PSF—Ar—NH_2 and (b) 160—PSF—Ar—NH_2.

2.5. Suzuki-Miyaura coupling reactions of other boron functionalized polysulfones ($PSF–B(OH)_2$ and $PSF–BF_3K$)

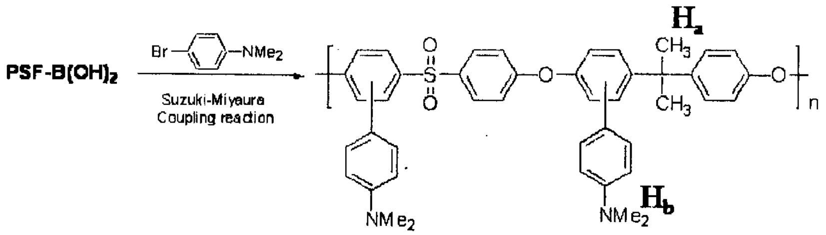
Potassium aryl trifluoroborate ($Ar-BF_3K$) and aryl boronic acid ($Ar-B(OH)_2$) are known for having higher reactivity than pinacol boronic ester in Suzuki-Miyaura coupling reactions.[35] Having polysulfones with other boron functionalities (i.e., $PSF–B(OH)_2$ and $PSF–BF_3K$) in hand, we also tested those polymers as intermediate polymer for various functionalized polysulfones by performing Suzuki-Miyaura coupling reactions with aryl halides under similar conditions as the PSF–Bpin. To demonstrate this possibility, Suzuki-Miyaura coupling reactions with $PSF–B(OH)_2$ and $PSF–BF_3K$ with *p*-bromo-N,N'-dimethylaniline under the similar condition of PSF-Bpin were performed in the presence of 3 mol% of $Pd(OAc)_2$, 3 mol% of Ru-Phos, and K_3PO_4 in a 1:10 mixture of ethanol and THF, giving the corresponding N,N'-dimethylaniline-functionalized polysulfones ($PSF–Ar'–NMe_2$ and $PSF–Ar''–NMe_2$ of Scheme 23). In principle, $PSF–Ar'–NMe_2$ and $PSF–Ar''–NMe_2$ are supposed to be identical to $PSF–Ar–NMe_2$, which was prepared from the coupling reaction of the corresponding PSF-Bpin.

The ^1H NMR spectra of $40–PSF–Ar'–NMe_2$ and $160–PSF–Ar'–NMe_2$ (Figure 24), which were prepared from Suzuki-Miyaura couplings of $40–PSF–Ar–B(OH)_2$ and $160–PSF–Ar–B(OH)_2$ respectively, showed the same NMR spectra of corresponding $PSF–Ar–NMe_2$ (Figure 19) that were prepared from PSF–Bpin, indicating the identical concentration of N,N'-dimethylaniline group was present. As shown in Figure 24 (a) and (b), the methyl resonance the N,N'-dimethylaniline group appeared at 2.9 ppm with a similar concentration to the methyl resonance of Bpin group of the PSF-Bpin. As the concentration of N,N'-dimethylaniline group increased in the polymers, this resonance was augmented [Figure 24 (a) and (b)].

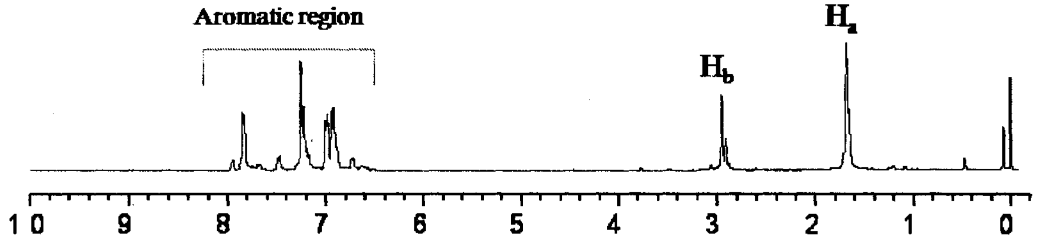


Scheme 23. Preparation of N,N'-dimethylaniline-functionalized polysulfones from Suzuki-Miyaura coupling reactions of other boron functionalized polysulfones (PSF—$B(OH)_2$ and PSF—BF_3K).

When ^1H NMR spectra of 40—PSF—Ar″—NMe_2 and 160—PSF—Ar″—NMe_2 (Figure 25), which were prepared from the Suzuki-Miyaura couplings of the corresponding PSF—Ar—BF_3K, were compared to the corresponding PSF—Ar—NMe_2 (Figure 19) or PSF—Ar′—NMe_2 (Figure 24), all the aniline-functionalized polysulfones were found to be identical, which indicates the same concentration of N,N'-dimethylaniline group was present regardless of the different boron functionalities in the precursor polymers. The methyl resonance of N, N-dimethylaniline group appeared at 2.9 ppm with a similar concentration of the methyl resonance of Bpin group of the PSF-Bpin. As the concentration of N,N'-dimethylaniline group increased in the polymers, the intensity of the resonance also increased.



(a) 40–PSF–Ar'–NMe$_2$ from 40–PSF–B(OH)$_2$



(b) 160–PSF–Ar'–NMe$_2$ from 160–PSF–B(OH)$_2$

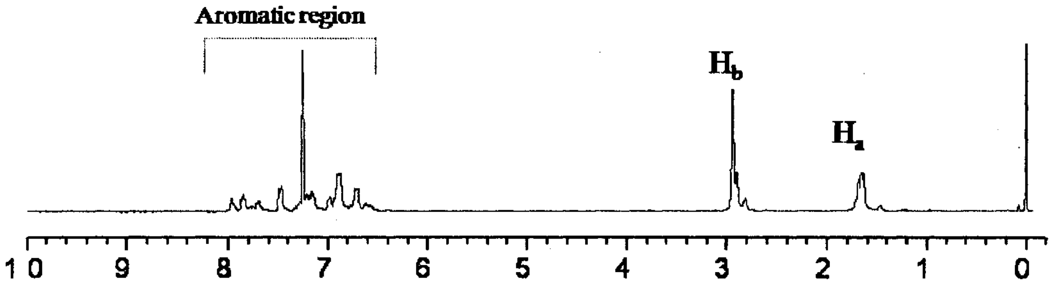
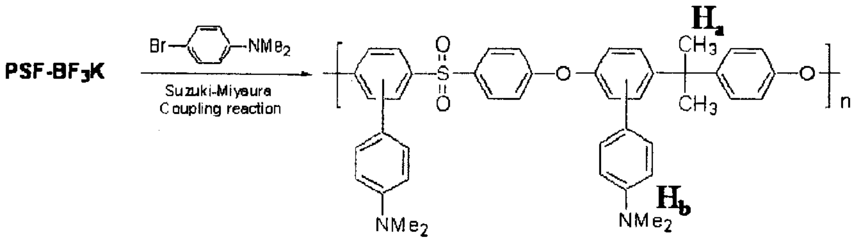
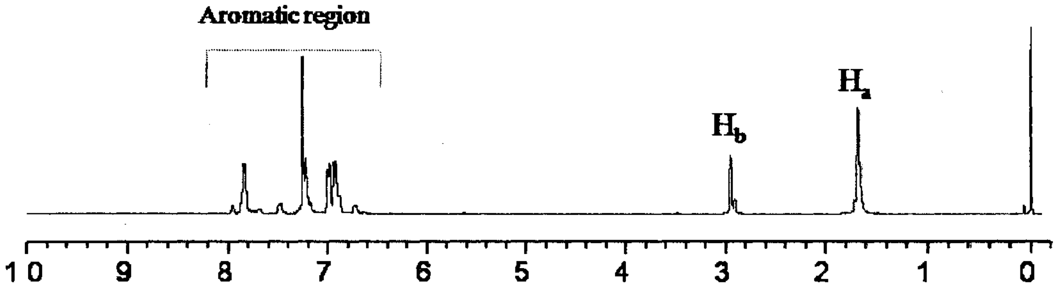


Figure 24. ^{1}H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–Ar'–NMe$_2$ and (b) 160–PSF–Ar'–NMe$_2$ from Suzuki-Miyaura couplings of the corresponding PSF–B(OH)$_2$ [10 mg/mL in CDCl$_3$ at 25°C].



(a) 40–PSF–Ar"–NMe$_2$ from 40–PSF–BF$_3$K



(b) 160–PSF–Ar"–NMe$_2$ from 160–PSF–BF$_3$K

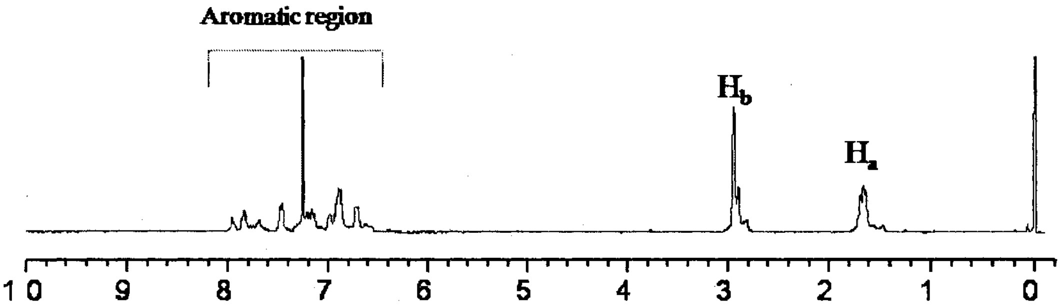


Figure 25. ^{1}H NMR spectra [delay time = 1s, number of transients = 16] of (a) 40–PSF–Ar″–NMe$_2$ and (b) 160–PSF–Ar″–NMe$_2$ prepared from Suzuki-Miyaura couplings of the corresponding PSF–BF$_3$K [10 mg/mL in CDCl$_3$ at 25°C].

Based on the analysis of ^{1}H NMR spectra of PSF–Ar′–NMe$_2$ and PSF–Ar″–NMe$_2$, we confirm that both PSF–B(OH)$_2$ and PSF–BF$_3$K, similar to PSF-Bpin, can serve as a versatile intermediate polymer that can be converted to other useful functional polysulfones.

2.6. Viscosity measurement

The inherent viscosity data of PSF, PSF–Bpin, PSF–OH, PSF–BF_3K, PSF–$B(OH)_2$, and the Suzuki–Miyaura coupling polymer products are summarized in Table 4. The viscosities of all the polymers were measured in DMAc except for PSF–BF_3K, where a 0.1M NaI in DMSO solution was used to reduce polyelectrolytic interactions between –BF_3K groups in the polymer. All polymers including unfunctionalized PSF showed inherent viscosities in the range of 0.52–0.61 dL/g. Considering the inherent viscosity of PSF (η_{inh} = 0.53 dL/g), it appears that no significant side reactions that can alter molecular weight of from the starting polymer occurred during the functionalization reactions.

Table 4. Inherent viscosity data of PSF–Bpin, PSF–OH, PSF–BF_3K, PSF–$B(OH)_2$, and the Suzuki coupling polysulfone products.[a]

entry	Functionalized Polysulfone	η_{inh} (dL/g)	entry	Functionalized polysulfone	η_{inh} (dL/g)
1	40–PSF–Bpin	0.54	11	160–PSF–Bpin	0.55
2	40–PSF–OH	0.53	12	160–PSF–OH	0.55
3	40–PSF–BF_3K^b	0.54	13	160–PSF–BF_3K^b	0.58
4	40–PSF–$B(OH)_2$	0.52	14	160–PSF–$B(OH)_2$	0.54
5	40–PSF–Ar–$COCH_3$	0.54	15	160–PSF–Ar–$COCH_3$	0.60
6	40–PSF–Ar–OTBDMS	0.54	16	160–PSF–Ar–OTBDMS	0.61
7	40–PSF–Ar–SO_3R	0.56	17	160–PSF–Ar–SO_3R	0.61
8	40–PSF–Ar–NMe_2	0.54	18	160–PSF–Ar–NMe_2	0.59
9	40–PSF–Ar–NH(Boc)	0.56	19	160–PSF–Ar–NH(Boc)	0.61
10	40–PSF–Ar–NH_2	0.54	20	160–PSF–Ar–NH_2	–[c]

[a] Unless otherwise stated, η_{inh} was measured in a DMAc solution at 30 °C with a concentration of 1.0 mg/mL (PSF: η_{inh} = 0.53 dL/g).

[b] Measured in a 0.1 M NaI solution in DMSO at 30 °C with a concentration of 1.0 mg/mL.

[c] Not measured due to insolubility in DMAc.

2.7. Differential scanning calorimetry (DSC) measurement

The thermal properties data of polysulfone (PSF) and functionalized PSFs (PSF—Bpin, PSF—OH, PSF—BF_3K, PSF—$B(OH)_2$, and PSF—Ar—NH_2) were studied using differential scanning calorimetry. As shown in table 5, all functionalized polysulfones showed increased glass transition temperature (T_g) compared to that of PSF and T_g of polymer samples with the same functionality increased as the mol % of functional group in polymer increased. The pinacol boronic ester-functionalized polysulfones (PSF—Bpin, entries 2 and 3 of table 5) exhibited an increased T_g compared to 190 °C of the unfunctionalized polysulfone (PSF, entry 1 of table 5) due to the incorporation of the bulky Bpin group into the polymer. The hydroxylated polysulfones (PSF—OH, entry 4 and 5 of table 5) displayed a higher T_g than that of polysulfone (PSF, entry 1 of table 5), since the presence of polar hydroxyl group enhanced both the polarity and T_g of the polymer through hydrogen bonding interaction. The introduction of an ionic functional group gives an significant increment of T_g because of the increased intermolecular association through the polar ionic sites.[5] Because potassium trifluoroborate functionalized polysulfones (PSF—BF_3K, entry 6 and 7 in table 5) have polar ionic sites along the polymer chain, these polymers showed much higher T_g in comparison with any other functionalized polysulfones in table 5. The boronic acid-functionalized polysulfones (PSF—$B(OH)_2$, entry 8 and 9 in table 5) showed a slightly increased T_g presumably both the polarity and hydrogen bonding interaction of boronic acid group. The aniline-functionalized polysulfones from the Suzuki-Miyaura coupling products (PSF—Ar—NH_2, entry 10 and 11 in table 5) displayed higher T_g than unfunctionalized polysulfone (PSF, entry 1 in table 5). This result implied that the introduction of aromatic spacer group induced the stiffening along the polymer chain instead of mobility induced from alkyl spacer group. The incorporation of polar primary amine group in the aniline could also contribute increase of T_g of the polymers.

Table 5. Thermal properties of polysulfone and functionalized polysulfones.[a]

Entry	Polymer	Functional group[b]	T_g (°C)[c]
1	PSF	None	190
2	40–PSF–Bpin	38 mol% Bpin	203
3	160–PSF–Bpin	146 mol% Bpin	217
4	40–PSF–OH	38 mol% OH	227
5	160–PSF–OH	146 mol% OH	235
6	40–PSF–BF_3K	38 mol% BF_3K	279
7	160–PSF–BF_3K	146 mol% BF_3K	287
8	40–PSF–$B(OH)_2$	38 mol% $B(OH)_2$	198
9	160–PSF–$B(OH)_2$	146 mol% $B(OH)_2$	207
10	40–PSF–Ar–NH_2	42 mol% NH_2[d]	204
11	160–PSF–Ar–NH_2	148 mol% NH_2[d]	234

[a] Differential scanning calorimetry (DSC) measurements conducted using heating/cooling rates of 10 °C/min.

[b] The mol % of functional groups in polymer was calculated based on the assumption of quantitative conversion of Bpin group without formation of any other deborylated byproducts.

[c] Glass transition temperature of polymer in °C and these values were obtained from second heating.

[d] The concentration of NH_2 group was derived from the concentration of NHBoc of the corresponding PSF-Ar-NHBoc from Table 3.

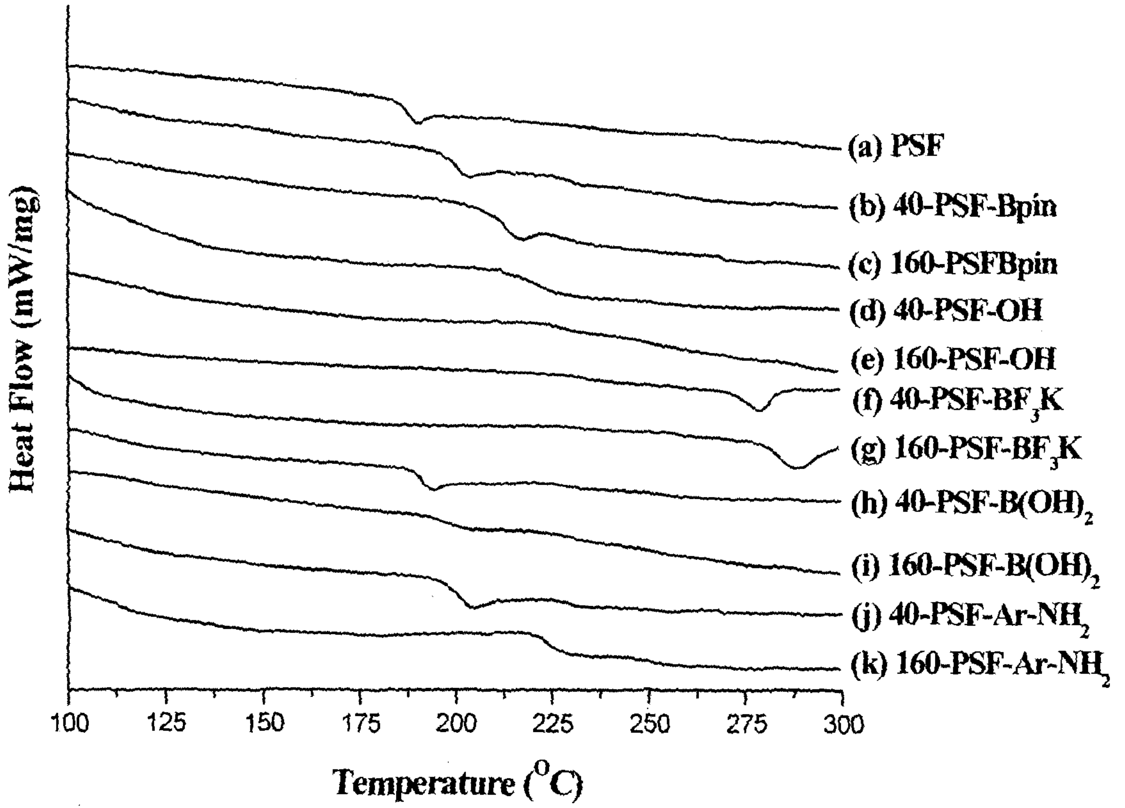


Figure 26. DSC scans of (a) PSF, (b) 40–PSF–Bpin, (c) 160–PSF–Bpin, (d) 40–PSF–OH, (e) 160–PSF–OH, (f) 40–PSF–BF$_3$K, (g) 160–PSF–BF$_3$K, (h) 40–PSF–B(OH)$_2$, (i) 160–PSF–B(OH)$_2$, (j) 40–PSF–NH$_2$, (k) 160–PSF–NH$_2$.

CHAPTER 3

EXPERIMENTAL SECTION

3.1. General comments

Udel® polysulfone (M_n = 22 kg/mol by membrane osmometry) was purchased from Aldrich Chemical Co. d*t*bpy, $[IrCl(COD)]_2$, $NaIO_4$, KHF_2, 4-bromoacetophenone, 4-bromo-N,N'-dimethylaniline, 4-bromo-N-*tert*-butoxycarbonylaniline, hydrogen peroxide, sodium hydroxide, tetrahydrofuran (THF), hexane, methanol, and chloroform were reagent grade and used without further purification. B_2pin_2 was obtained from Frontier Scientific Co. and used after recrystallization from hexane.

^1H NMR spectra were obtained using a 400 MHz Varian NMR spectrometer at room temperature and chemical shifts were referenced to TMS. The ^1H NMR samples were prepared with gentle heat to dissolve the polymers in $CDCl_3$ (for PSF–Bpin and the Suzuki–Miyaura coupling polymer products) and DMSO-d_6 (for PSF–OH, PSF–BF_3K, and PSF–$B(OH)_2$) at a concentration of 10 mg/1 mL. ^{13}C NMR spectra were obtained using a 100 MHz Varian NMR spectrometer at room temperature and chemical shifts were referenced to TMS. The ^{13}C NMR samples were prepared by applying gentle heat to dissolve 40 mg of the polymer in 1 mL of NMR solvent. ^{11}B NMR spectra were obtained using a 128 MHz Varian NMR spectrometer at room temperature and chemical shifts were referenced to BF_3-OEt_2. The ^{11}B NMR samples were measured in a quartz tube and they were prepared by applying gentle heat to dissolve 40 mg of polymer in 1 mL of $CDCl_3$ (for PSF–Bpin) or DMSO-d_6 (for PSF–BF_3K and PSF–$B(OH)_2$). ^{19}F NMR spectra were obtained using a 376 MHz Varian NMR spectrometer at room temperature and chemical shifts were referenced to $CFCl_3$. The NMR samples were prepared by applying gentle heat to dissolve 10 mg of PSF–BF_3K in 1 mL of DMSO-d_6.

For PSF, PSF–Bpin, PSF–OH, PSF–$B(OH)_2$, and the Suzuki–Miyaura coupling products, the inherent viscosities of polymer products were measured using an Ubbelohde capillary viscometer at 30 °C in DMAc solution with a concentration of 1.0 mg/mL. To eliminate polyelectrolyte effect in dilute solution of ionic polymer, the inherent viscosity of PSF–BF_3K was measured in a 0.1 M NaI solution of DMSO at 30 °C with a concentration of 1.0 mg/mL.

The differential scanning calorimetry (DSC) was conducted on a NETZSCH STA 449C under a helium atmosphere. The polymer samples were heated to 300 °C, held at 300 °C for 1 min to remove the influence of the thermal history, cooled down to 0 °C, held at 0 °C for 1 min, and then reheated to 300 °C with 10 °C/min heating and cooling rates for all samples. All DSC data shown in Figure 26 were obtained from the second heating.

Udel® Polysulfone

^1H NMR (400 MHz, $CDCl_3$) (Figure 3a) = 1.69 (s, 6H, CH_3), 6.95 (d, 4H, H_{arom}, J = 8.8 Hz), 7.01 (d, 4H, H_{arom}, J = 8.8 Hz), 7.25 (d, 4H, H_{arom} J = 8.8 Hz), 7.86 (d, 4H, H_{arom}, J = 8.8 Hz). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) (Figure 4a) = 31.2 [$C(\mathit{C}H_3)_2$], 42.6 [$\mathit{C}(CH_3)_2$], 117.9, 120.0, 128.7, 129.9, 135.6, 147.4, 153.1, 162.2 (all from C_{arom}).

3.2. Preparation of pinacol boronic ester-functionalized polysulfone

(40–PSF–Bpin)

Polysulfone (11.05 g, 25 mmol of polysulfone repeating unit), B_2pin_2 (2.5 g, 10 mmol), $[IrCl(COD)]_2$ (100.8 mg, 3 mol% of B_2pin_2 based on iridium atom), d*t*bpy (80.4 mg, 3 mol% of B_2pin_2) and THF (60 mL) were added to a round-bottom flask in a nitrogen filled glove box. The flask was removed from the glove box and the mixture was refluxed at 80 °C for 12 h under nitrogen. After cooling down to room temperature, the reaction mixture was diluted with THF (300 mL) and filtered through a plug of silica gel to remove the catalyst. After evaporation of the solvent to about 30 mL, hexane (100 mL) was added to precipitate. The process of dissolution in THF and precipitation with hexane was repeated one more time to ensure all small molecules are removed. The polymer product was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (12.05 g, 109% yield based on polymer weight). ^1H NMR (400 MHz, $CDCl_3$) (Figure 3b) = 1.03 and 1.23 ($\mathrm{BOCC}H_3$ of Bpin), 1.60–1.74 (6H, $\mathrm{C}(\mathrm{C}H_3)_2$ of the polysulfone main chain), 6.80–7.04 (H_{arom}), 7.14–7.30 (H_{arom}), 7.72–7.92 (H_{arom}), 8.26–8.34 (H_{arom}). $^{13}C\ \{^1H\}$ NMR (100 MHz, $CDCl_3$) (Figure 4b) = 24.8–24.6 ($\mathrm{BOC}(CH_3)$ of Bpin), 30.9 ($\mathrm{C}(CH_3)_2$ of the polysulfone main chain), 42.1–42.5 ($C(\mathrm{CH}_3)_2$ of the polysulfone main chain), 83.7–84.2 ($\mathrm{BO}C(\mathrm{CH}_3)$ of Bpin), 114–166 (multiple C_{arom}).

3.3. Preparation of hydroxy-functionalized polysulfone

(40–PSF–OH)

The pinacol boronic ester-functionalized polysulfone (40–PSF–Bpin) (500 mg) was dissolved in THF (200 mL) at room temperature. A mixture of 3M NaOH (1 mL) and 30 mol % H_2O_2 (1 mL) was slowly added to the polymer solution dropwise and the reaction mixture was stirred for 12 h at room temperature. After evaporation of solvent to about 5 mL, a mixture of cold methanol (20 mL) and water (80 mL) was added to precipitate the polymer. The resulting heterogeneous suspension was stirred for 30 min and polymer product was obtained by filtration and drying under vacuum at 80 °C (465 mg, 93% yield base on polymer weight). ^{1}H NMR (400 MHz, DMSO-d_6) (Figure 6a) = 1.4–1.7 (6H, C(CH_3)$_2$ of the polysulfone main chain), 6.5–8.0 (multiple H_{arom}). FT-IR (KBr pellet) (Figure 7a) υ = 3447 cm^{-1} (O—H stretching). ^{13}C {^{1}H} NMR spectrum was not recorded due to poor solubility of the polymer in the NMR solvent.

3.4. Preparation of potassium trifluoroborate-functionalized polysulfone (40—PSF—BF_3K)

The pinacol boronic ester-functionalized polysulfone (40—PSF—Bpin) (500 mg) was dissolved in THF (200 mL) at room temperature. An aqueous solution of KHF_2 (320 mg in 2 mL) was added the polymer solution dropwise and the reaction mixture was stirred for 12 h at room temperature. After evaporation of solvent to about 5 mL, a mixture of cold methanol (20 mL) and water (80 mL) was added to precipitate the polymer. The resulting heterogeneous suspension was stirred for 10 min. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (475 mg, 95% yield base on polymer weight). ^{1}H NMR (400 MHz, DMSO-d_6) (Figure 11a) = 1.4–1.7 (6H, C(CH_3)$_2$ of the polysulfone main chain), 6.5–8.3 (multiple H_{arom}). ^{19}F NMR (376 MHz, DMSO-d_6) (Figure 13a) = –137.2, –138.5. ^{13}C {^{1}H} NMR spectrum was not recorded due to poor solubility of the polymer in the NMR solvent.

3.5. Preparation of boronic acid-functionalized polysulfone
(40–PSF–B(OH)$_2$)

The pinacol boronic ester-functionalized polysulfone (40–PSF–Bpin) (500 mg) was dissolved in THF (200 mL) at room temperature. An aqueous solution of NaIO$_4$ (170 mg in 2 mL) was added the polymer solution dropwise and the reaction mixture was stirred for 12 h at room temperature. After evaporation of solvent to about 5 mL, a mixture of cold methanol (20 mL) and water (80 mL) was added to precipitate the polymer. The resulting heterogeneous suspension was stirred for 30 min. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (455 mg, 91% yield base on polymer weight). ^{1}H NMR (400 MHz, DMSO-d$_6$) (Figure 8a) = 1.4–1.7 (6H, C(CH_3)$_2$ of the polysulfone main chain), 6.5–8.3 (multiple H$_{\text{arom}}$). FT-IR (KBr pellet) (Figure 10a) υ = 3503 cm^{-1} (O–H stretching). ^{13}C {^{1}H} NMR spectrum was not recorded due to poor solubility of the polymer in the NMR solvent.

3.6. Preparation of Suzuki–Miyaura cross coupled products

3.6.1. Preparation of acetophenone-functionalized polysulfone
(40–PSF–Ar–COCH$_3$)

In a nitrogen-filled glovebox, 40–PSF–Bpin (246 mg, 0.5 mmol Bpin in the polymer), 4-bromoacetophenone (199 mg, 1 mmol), Pd(OAc)$_2$ (1.3 mg, 3 mol % based on the amount of boron concentration in PSF–Bpin), XPhos (2.9 mg, 3 mol % based on the amount of boron concentration in PSF–Bpin), and K$_2$CO$_3$ (83 mg, 3 equiv based on the amount of boron concentration of PSF–Bpin), a mixture of THF (2 mL) and water (0.2 mL), and a magnetic stirring bar were added into a vial. The vial was capped with

Teflon-lined septum, removed from the glovebox, and placed in an 80 °C oil bath for 6 h. After cooling to room temperature, the mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporation to about 3 mL and cold methanol (15 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure all small molecules are removed. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (230 mg, 93% yield based on polymer weight). ^{1}H NMR (400 MHz, $CDCl_3$) (Figure 14a) = 1.6–1.80 (6H, $C(CH_3)_2$ of the polysulfone main chain), 2.50–2.65 (3H, CH_3 of acetophenone), 6.6–8.0 (multiple H_{arom}). FT-IR (film) (Figure 15a) υ = 1684 cm^{-1} (C=O stretching of acetophenone).

3.6.2. Preparation of *tert*-butyldimethylsiloxyphenyl-functionalized polysulfone (40–PSF–Ar–OTBDMS)

In a nitrogen-filled glovebox, 40–PSF–Bpin (246 mg, 0.5 mmol Bpin in the polymer), 4-bromophenoxy-*tert*-butyldimethylsilane (287 mg, 1 mmol), $Pd(OAc)_2$ (1.3 mg, 3 mol % based on the amount of boron concentration in PSF–Bpin), XPhos (2.9 mg, 3 mol % based on the amount of boron concentration in PSF–Bpin), and K_3PO_4 (127.4 mg, 3 equiv based on the amount of boron concentration of PSF–Bpin), a mixture of THF (2 mL) and ethanol (0.2 mL), and a magnetic stirring bar were added into a vial. The vial was capped with Teflon-lined septum, removed from the glovebox, and placed in an 80 °C oil bath for 6h. After cooling to room temperature, the reaction mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporation to about 3 mL and cold methanol (15 mL) was added into to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure all small molecules are removed. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (200 mg, 81% yield based on polymer weight). ^{1}H NMR (400MHz, $CDCl_3$) (Figure 16a). = 0.15–0.25 (6H, $Si(CH_3)_2$ of OTBDMS), 0.90–1.00 (9H, *t*-butyl group of OTBDMS),1.60–1.75 (6H, $C(CH_3)_2$ of the polysulfone main chain), 6.6–8.0 (multiple H_{arom}).

3.6.3. Preparation of neopentyl arylsulfonate ester-functionalized polysulfone (40–PSF–Ar–SO_3R)

In a nitrogen-filled glovebox, 40–PSF–Bpin (246mg, 0.5 mmol Bpin in the polymer), neopentyl 4-bromophenylsulfonate ester§ (307 mg, 2 mmol), $Pd(OAc)_2$ (1.3 mg, 3 mol % based on the amount of boron concentration in PSF–Bpin), XPhos (2.9 mg, 3 mol % based on the amount of boron concentration in PSF–Bpin), and K_2CO_3 (83 mg, 3 equiv based on the amount of boron concentration of PSF–Bpin), a mixture of THF (2 mL) and water (0.2 mL), and a magnetic stirring bar were added into a vial. The vial was capped with Teflon-lined septum, removed from the glovebox, and placed in an 80 °C oil bath for 6 h. After cooling to room temperature, the reaction mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporation to about 3 mL and cold methanol (15 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure all small molecules are removed. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (220 mg, 89% yield based on polymer weight). ^{1}H NMR (400MHz, $CDCl_3$) (Figure 17a) = 0.80–0.95 (9H, *t*-butyl of neopentyl group), 1.60–0.75 (6H, $C(CH_3)_2$ of the polysulfone main chain), 3.60–

3.80 (2H, CH_2 of neopentyl group), 6.6–8.0 (multiple H_{arom}). FT-IR (film) (Figure 18a) $\upsilon = 964\ cm^{-1}$ (S—O stretching in ester).

§Preparation of neopentyl 4-bromophenylsulfonate ester

Chlorosulfonic acid (8 mL, 120 mmol) was slowly added into a capped vial containing p-bromobenzene (2 mL, 20 mmol) in an ice bath and heated at 50 °C for 3 h. The cap of the vial was perforated with a needle to release the pressure inside the vial. The reaction mixture was quenched with ice and extracted with methylene chloride. The organic layer was washed with water and aqueous $NaHCO_3$ solution and dried over $MgSO_4$. The crude organic solution containing 4-bromophenylsulfonyl chloride was added into dry pyridine solution (4.9 mL, 60 mmol) of neopentyl alcohol (2.6 g, 30 mmol) and stirred for 48 h at room temperature. The reaction mixture was washed with 0.1% aqueous HCl solution (30 mL × 3), brine (30 mL × 3), and water (30 mL × 3), and dried over $MgSO_4$. The product was obtained as a white crystal after two times of recrystallization from hexane (Yield = 3.5 g, 57 %). ^1H NMR (400 MHz, $CDCl_3$) = 7.76 (d, 2H, H_{arom}, J = 8.8 Hz), 7.69 (d, 2H, H_{arom}, J = 8.8 Hz), 3.67 (s, 2H, CH_2), 0.88 (s, 9H, $C(CH_3)_3$). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) = 26.2 [$C(\underline{C}H_3)_4$], 31.9 [$\underline{C}(CH_3)_2$], 80.2($\underline{C}H_2$ of neopentyl ester), 129.1, 129.6 (×2), 132.8 (×2), 135.3 (all from C_{arom}).

3.6.4. Preparation of N, N-dimethylaniline-functionalized polysulfone (40—PSF—Ar—NMe_2)

In a nitrogen-filled glovebox, 40—PSF—Bpin (246 mg, 0.5 mmol Bpin in the polymer), 4-bromo-N,N'-dimethylaniline (120 mg, 1 mmol), $Pd(OAc)_2$ (1.3 mg, 3 mol % based on the amount of boron concentration in PSF—Bpin), RuPhos (2.8 mg, 3 mol % based on the amount of boron concentration in PSF—Bpin), and K_3PO_4 (127.4 mg, 3 equiv based on the amount of boron concentration of PSF–Bpin), a mixture of THF (2 mL) and ethanol (0.2 mL), and a magnetic stirring bar were added into a vial. The vial was capped with Teflon-lined septum, removed from the glovebox, and placed in an oil bath at 80 °C for 6 h. After cooling to the room temperature, the reaction mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporation to about 3 mL and cold methanol (15 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of all small molecules. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (225 mg, 91% yield based on polymer weight). ^1H NMR (400MHz, $CDCl_3$) (Figure 19a) = 1.60–1.75 (6H, $C(CH_3)_2$ of the polysulfone main chain), 2.80–3.00 (6H, $N(CH_3)_2$), 6.6–8.0 (multiple, H_{arom}).

3.6.5. Preparation of N-tert-butoxycarbonylaniline-functionalized polysulfone (40–PSF–Ar–NHBoc)

In a nitrogen-filled glovebox, 40–PSF–Bpin (246 mg, 0.5 mmol Bpin in the polymer), 4-bromo-N-*tert*-butoxycarbonylaniline (272 mg, 1 mmol), $Pd(OAc)_2$ (1.3 mg, 3mol% based on the amount of boron concentration in PSF–Bpin), RuPhos (2.8 mg, 3 mol % based on the amount of boron concentration in PSF–Bpin), and K_3PO_4 (127.4 mg, 3 equiv to the amount of boron concentration of PSF–Bpin), a mixture of THF (2 mL) and ethanol (0.2 mL), and a magnetic stirring bar were added into a vial. The vial was capped with Teflon-lined septum, removed from the glovebox, and placed in an oil bath at 80 °C for 6 h. After cooling to room temperature, the reaction mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporation to about 3 mL and cold methanol (15 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal all small molecules. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (225 mg, 91% yield based on polymer weight). ^{1}H NMR (400 MHz, $CDCl_3$) (Figure 20a) = 1.40–1.55 (9H, *t*-butyl group of N-*tert*-butoxycarbonylaniline), 1.60–1.75 (6H, $C(CH_3)_2$ of the polysulfone main chain), 6.6–8.0 (multiple H_{arom}). FT-IR (film) (Figure 21a) υ =3358 cm^{-1} (N—H stretching vibration of NHBoc), 1729 cm^{-1} (C=O stretching of NHBoc), 1585 cm^{-1} (N—H bending vibration of NHBoc).

3.6.6. Preparation of aniline-functionalized polysulfone

(40—PSF—Ar—NH_2)

N-*tert*-Butoxycarbonylaniline-functionalized polysulfone (40—PSF—Ar—NHBoc) (52 mg, 0.04 mmol NHBOC group in the polymer) was added into $CHCl_3$ (5 mL). Trifluoroacetic acid (0.15 mL) was added to the mixture dropwise at room temperature with stirring. After 60 h, the reaction mixture was concentrated by rotary evaporation to about 1 mL and cold methanol (5 mL) was added to precipitate the polymer. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (46 mg, 88% yield based on polymer weight). ^{1}H NMR (400 MHz, $CDCl_3$) (Figure 22) = 1.60–1.75 (6H, $C(CH_3)_2$ of the polysulfone main chain), 6.6–8.0 (multiple H_{arom}). FT-IR (film) (Figure 23a) υ =3480 cm^{-1} (asymmetric N—H stretching of NH_2), 3383 cm^{-1} (symmetric N—H stretching of NH_2), 1587 cm^{-1} (N—H bending vibration of NH_2).

3.6.7. Preparation of N,N'-dimethylaniline-functionalized polysulfone from boronic acid-functionalized polysulfone (40–PSF–Ar'–NMe$_2$)

In a nitrogen-filled glovebox, 40–PSF–B(OH)$_2$ (92 mg, 0.2 mmol B(OH)$_2$ in the polymer), 4-bromo-N,N'-dimethylaniline (80 mg, 0.4 mmol), Pd(OAc)$_2$ (0.54 mg, 3 mol % based on the amount of boron concentration in PSF–B(OH)$_2$), RuPhos (1.1 mg, 3 mol % based on the amount of boron concentration in PSF–B(OH)$_2$), and K$_3$PO$_4$ (51 mg, 3 equiv to the amount of boron concentration of PSF–B(OH)$_2$), a mixture of THF (2 mL) and ethanol (0.2 mL), and a magnetic stirring bar were added into a vial. The vial was capped with Teflon-lined septum, removed from the glovebox, and placed in an oil bath at 80°C for 12 h. After cooling to the room temperature, the reaction mixture was diluted with chloroform (20 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporation to about 2 mL and cold methanol (10 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of all small molecules. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (90 mg, 98 % yield based on polymer weight). ^{1}H NMR (400 MHz, CDCl$_3$) (Figure 24a) = 1.60–1.75 (6H, C(CH_3)$_2$ of the polysulfone main chain), 2.80–3.00 (6H, N(CH_3)$_2$), 6.6–8.0 (multiple H$_{arom}$).

3.6.8. Preparation of N,N'-dimethylaniline-functionalized polysulfone from potassium trifluoroborate functionalized polysulfone (40–PSF–Ar''–NMe$_2$)

In a nitrogen-filled glovebox, 40–PSF–BF$_3$K (97 mg, 0.2 mmol BF$_3$K in the polymer), 4-bromo-N,N'-dimethylaniline (80 mg, 0.4 mmol), Pd(OAc)$_2$ (0.54 mg, 3 mol % based on the amount of boron concentration in PSF–BF$_3$K), RuPhos (1.1 mg, 3 mol % based on the amount of boron concentration in PSF–BF_3K), and K_3PO_4 (51 mg, 3 equiv to the amount of boron concentration of PSF–BF_3K), a mixture of THF (1 mL) and ethanol (0.1 mL), and a magnetic stirring bar were added into a vial. The vial was capped with Teflon-lined septum, removed from the glovebox, and placed in an oil bath at 80°C for 12 h. After cooling to the room temperature, the reaction mixture was diluted with chloroform (20 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporation to about 2 mL and cold methanol (10 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of all small molecules. The polymer was obtained as an off-white solid after filtration and drying under vacuum at 80 °C (80 mg, 82% yield based on polymer weight). ^1H NMR (400 MHz, $CDCl_3$) (Figure 25a) = 1.60–1.75 (6H, $C(CH_3)_2$ of the polysulfone main chain), 2.80–3.00 (6H, $N(CH_3)_2$), 6.6–8.0 (multiple H_{arom}).

CHAPTER 4

CONCLUSION

Iridium catalyzed aromatic C–H bond activation/ funcitonalization of polysulfone with B_2pin_2 introduced the pinacol boronic ester functionality without significantly affecting the polymer chain length. The degree of functionalization of polysulfone could be easily controlled by changing the ratio of diboron reagent to repeating units in the iridium-catalyzed borylation. The pinacol boronic ester-functionalized polysulfone (PSF—Bpin) has a potential to be used as a versatile precursor for introducing various functional groups via simple transformation reactions and Suzuki-Miyaura cross coupling reaction. We demonstrated that the Bpin functional group on the polysulfone could be converted to other functionalities with a similar concentration of the starting polymer. Subsequent transformation reactions of PSF—Bpin produced the hydroxylated (–OH), potassium trifluoroborate ($-BF_3K$), and boronic acid ($-B(OH)_2$) functional groups on the aromatic ring of polysulfone. In addition, PSF–Bpin could be converted to various polar functional groups, including ketone, silane, sulfonated ester, amine, and amide, via one-step Suzuki-Miyaura cross coupling reaction under mild condition. With this mild method, we successfully incorporated various polar functional groups into the aromatic ring of polysulfone. Since aryl boron compounds containing potassium trifluoroborate ($-BF_3K$), and boronic acid ($-B(OH)_2$) have a possibility to be used as substrate in Suzuki-

Miyaura coupling reaction, we also demonstrate that boronic acid-functionalized polysulfone (PSF–$B(OH)_2$) and potassium trifluoroborate-functionalized polysulfone (PSF–BF_3K) could be converted to the dimethylaniline-functionalized polysulfones via Suzuki-Miyaura coupling reaction. The results of all functionalized polysulfone products were confirmed based on the ^1H NMR, ^{13}C NMR, and FT-IR spectra and thermal properties of the polymers were measured by differential scanning calorimetry (DSC). The viscosity measurement data indicated that no functionalized polymer products showed a significant change in their molecular weights from that of the starting polymer.

In summary, we synthesized a series of polar functionalized polysulfones via a combination of the iridium catalyzed aromatic C–H borylation and Suzuki-Miyaura cross coupling reaction without negatively affecting the polymer's chain length. This highly efficient and mild post-funcitonalization method can be conveniently used for the preparation of various functionalized polysulfones, which ultimately leads to broader applications of polysulfone-based engineering plastic materials.

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VITA

Graduate College
University of Nevada, Las Vegas

Se Hye Kim

Local Address:
5055 Lindell Rd. Unit 2082
Las Vegas, NV 89118

Home Address:
109-302 Mido Apt. Daechidong Kangnamgu
Seoul, South Korea, 135-282

Degree:
Bachelor of Science, Chemistry, 2002
Ewha Womans University, Seoul, South Korea

Master of Science, Chemistry, 2004
Ewha Womans University, Seoul, South Korea

Thesis Title: Post-modification of polysulfone using transition metal catalyzed C-H activation and Suzuki-Miyaura cross couplingreaction.

Thesis Examination Committee:
Chairperson, Dr. Chulsung Bae, Ph.D
Committee Member, Dr. Clemens Heske, Ph.D
Committee Member, Dr. Ernesto Abel-Santos, Ph.D
Graduate Faculty Representative, Dr. James Selser, Ph.D