I. Facile Friedel-Crafts Type Ring Closure Using Room Temperature Ionic Liquids in The Absence of Lewis Acid Catalyst.

II. Nucleophilic Substitution Reactions Using Polymer-supported Ionic Liquid: Ionic Resins.

2005 년 2 월

仁荷大學校 大學院 化學科 (化學專攻)
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I. 이온성 액체를 이용한 Friedel-Crafts형태의 고리화반응
II. 폴리머에 결합된 이온성 액체의 친핵성 치환반응

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指導敎授 池 大 潤

이 論文을 碩士學位 論文으로 提出함

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化學科 (化學專攻)

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이 논문을洪東進의碩士學位論文으로認定함

2005년2월

主審_________________(인)

副審_________________(인)

副審_________________(인)
Contents

Part I. Facile Friedel-Crafts Type Ring Closure Using Room Temperature Ionic Liquids in The Absence of Lewis Acid Catalyst

Abstract (English) 2
Abstract (Korean) 3
I. Introduction 4
II. Results and Discussion 7
   1. The Preparation of Model Compounds.
   2. Cyclization under Various Reaction Conditions
   3. Cyclization of Various Substrates.
III. Conclusion 12
IV. Experiment 13
V. Reference 22
VI. Spectra Data 23


Abstract (English) 47
Abstract (Korean) 48
I. Introduction 49
II. Results and Discussion


2. Nucleophilic Substitutions with Various Length of Linker of Ionic Resins.

3. Fluorinations and Acetylation with Various Counter Anion of Ionic Resins.

4. Nucleophilic Substitutions Using Various Loading Level PS[hmim][BF₄].

5. Swelling Constants of Ionic Resins; PSIL (mL/g)

6. Fluorinations and Acetylation Using PS[hmim][BF₄] in Various Solvents

III. Conclusion

IV. Experiment

V. Reference
Part I. Facile Friedel-Crafts Type Ring Closure
Using Room Temperature Ionic Liquids in The
Absence of Lewis Acid Catalyst.
Abstract


The facile Friedel-Crafts type cyclizations of primary alkyl mesylate of aromatic compounds in the ionic liquids have been investigated without acidic catalyst. Reactions in ionic liquid not only enhance the reactivity of aromatic alkyl mesylate but also enhance selectivity. Among these reactions, cyclization of 2-(3-methanesulfonyloxypropoxy)naphthalene to 2,3-dihydro-1H-naphtho[2,1-b]pyran in 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) proceeded selectively at 150 °C for 24 h in 85% yield.
요약문

Part I. 이온성 액체를 이용한 고리화 반응

산 촉매를 사용하지 않고 이온성 액체 존재 하에서 새로운 Friedel-Crafts 형태의 고리화반응을 발견하였다. 이 이온성 액체 반응은 aromatic alkyl mesylate의 고리화반응의 반응성을 증가시켰을 뿐만 아니라 선택성도 향상시킨 것을 볼 수 있었다. 최적화된 이 고리화 반응조건을 연구하기위해 모델화합물로서 2-(3-메탄술포닐옥시프로폭시)나프탈렌을 사용하였다. 이온성 액체인 1-n-부틸-3-메틸이미다졸리움 헥사플루오르 포스페이트(\([\text{bmim}]\[\text{PF}_6]\))를 용매겸 촉매로 하여 150 ºC 에서 24시간을 반응시켜 고리화 반응이 85%의 수율로 2-(3-디하이드로-1H-나프토[2,1-b]피란을 얻었다.
I. Introduction

Ionic Liquid.

Ionic liquids are recently regarded as an eco-friendly alternative to replace volatile organic solvents in current chemical processing, due to their unique physical and chemical properties such as high ionic conductivity, non-volatile, non-flammable, high thermal stability, wide temperature range for liquid phase, highly solvating, yet non-coordinating and good solvent for many organic and inorganic materials.\(^1\) It has also been reported that ionic liquids containing imidazolium cations can act as powerful media in some of catalytic organic reactions not only for facilitating of catalyst recovery and but also for accelerating reaction rate and improving selectivity.\(^2\)

\[
\text{[bmim][X]} \ (X = BF_4, PF_6, SbF_6, OTf, NTf_2)
\]

**Figure 1.** Ionic liquids

Furthermore, a bi- or triphasic system caused by the immiscibility of some ionic liquids with some solvents – water, ether, hexane, benzene, etc. – provides facile purification and extraction of the desired products from ionic liquids.\(^{1a,3}\)

Synthesis of Chromane Compound.

Compounds bearing the chromane moiety are widespread in nature and have received much interest because of their physiological properties.\(^3\) The ring closure
cyclization of various aromatic ethers or alkyl phenols is the typical method for the preparation of chromanes. 5,6 (Figure 1)

![Diagram](https://via.placeholder.com/150)

**Figure 1.** The typical method of preparation of chromane.

Although the cyclization of alkyl phenols is easier reaction as shown B route (Figure 1) than that of ethers, the preparation of phenols as a starting material is not easy. On the other side, the cyclization of the various sulfony- and halopropyl ethers which were prepared easily, need the C-C bond formation as shown A route (Figure 1). Friedel-Crafts type ring closure alkylation is the most common method for these purposes. However, this reaction requires the vigorous reaction condition in the presence of strong Lewis acid.

This C-C bond formation reaction can be a nucleophilic substitution through π-electron on aromatic of the sulfony- and halopropyl aryl ethers as a nucleophile attacking to α carbon themselves. Nucleophilic substitution reactions are affected largely by solvent, the microenvironment created by the solvent can alter the outcome of these reactions in terms of both rate and equilibrium. In our recent report, it has successfully been developed novel reaction methods involving nucleophilic substitution type reactions performed in the presence of ionic liquids using various nucleophile sources and also obtained superior results compared with those of previous methods.

Ionic liquids containing imidazolium cations and their counter anions (see Figure 2) are attracting growing interest as an eco-friendly alternative to replace volatile organic solvents in current chemical processing, due to their unique chemical and physical properties – low vapor pressure, high thermal stability, long
range liquid area, and ease of handling.\textsuperscript{1} It has also been reported that ionic liquids can be used as powerful media in some catalytic organic reactions for the facilitation of catalyst recovery as well as for the acceleration of reaction rate and improvement of selectivity.\textsuperscript{7} Also, a number of nucleophilic displacement reactions have been reported in these new media. Boon et al. reported Friedel-Crafts alkylation reaction using 1-methy-3-ethylimidazolium chloride-aluminum(III) chloride ([emim]Cl–AlCl\textsubscript{3}) as both reaction media and Lewis acid. However, these reactions proceed still under strong acidic condition.\textsuperscript{8}

In this paper, it was presented a highly efficient method for the Friedel-Crafts type ring closure alkylation using various ionic liquids in absence of Lewis acid. It has also been investigated the reactivity of other leaving group such as bromide, chloride, fluoride, iodide, tosylate and secondary compound in [bmim][PF\textsubscript{6}].

\[
\begin{array}{c}
\text{[bmim]}[X] \quad X = BF_4, PF_6, SbF_6, OTf, NTf_2
\end{array}
\]

\textbf{Figure 2. Ionic Liquids}
II. Results and Discussion

The Preparation of Model Compounds.

Scheme 1.

OH
Br

OH
O

OMs

O
B

\[ \text{Reaction conditions: (a) K}_2\text{CO}_3, \text{acetone, reflux, 2 days, 92 \%}; (b) (\text{CH}_3\text{SO}_2)\text{O}, \text{TEA, CH}_2\text{Cl}_2, \text{rt, 1 h, 95 \%}; (c) TBABr, \text{CH}_3\text{CN, reflux, 3 h, 95 \%}. \]

Cyclization under Various Reaction Conditions.

After detailed investigation under various condition in ionic liquids, it was found that the use of the [bmim][PF_6] without Lewis acid such as ZnCl_2 gave good results. The results are summarized in Table 1.

The cyclization reaction of 2-(3-bromopropyl)naphthalene 2 under Lewis acid (1,4-dioxane, AlCl_3, 150 °C; entry 9) proved only trace amounts of 2,3-dihydro-1H-naphtho[2,1-b]pyran after 48 h, whereas the same reaction in [bmim][BF_4] without Lewis acid converted 54% in only 12 h (entry 1). The low conversion in entry 1 can be ascribed to dealkylation 3b. To remove the HBr, NaHCO_3 as base was used. But the reaction gave byproduct such as hydroxylation compound 3c (entry 2).
Table 1. Cyclization of Mesyl aAlkane A under Various Reaction Condition.$^a$

![Diagram of cyclization process]

<table>
<thead>
<tr>
<th>entry</th>
<th>ionic liquid</th>
<th>X</th>
<th>reaction time (h)</th>
<th>base or acid</th>
<th>temp. ($^\circ$C)</th>
<th>yield of product (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>[bmim][BF$_4$]</td>
<td>Br</td>
<td>12</td>
<td></td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td>2$^c$</td>
<td>[bmim][BF$_4$]</td>
<td>Br</td>
<td>24</td>
<td>NaHCO$_3$</td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>[bmim][BF$_4$]</td>
<td>OMs</td>
<td>48</td>
<td></td>
<td>150</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>[bmim][OTf]</td>
<td>OMs</td>
<td>24</td>
<td></td>
<td>150</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>[bmim][PF$_6$]</td>
<td>OMs</td>
<td>24</td>
<td></td>
<td>150</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>[bmim][SbF$_6$]</td>
<td>OMs</td>
<td>33</td>
<td></td>
<td>150</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>[bmim][NTf$_2$]</td>
<td>OMs</td>
<td>31</td>
<td></td>
<td>150</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>[bmim][PF$_6$]</td>
<td>OMs</td>
<td>24</td>
<td></td>
<td>110</td>
<td>67</td>
</tr>
<tr>
<td>9$^d$</td>
<td>1,4-dioxane</td>
<td>Br</td>
<td>48</td>
<td>AlCl$_3$ (3)</td>
<td>reflux</td>
<td>71</td>
</tr>
<tr>
<td>10$^d$</td>
<td>1,4-dioxane</td>
<td>Br</td>
<td>36</td>
<td>ZnCl$_2$ (3)</td>
<td>reflux</td>
<td>trace</td>
</tr>
<tr>
<td>11$^d$</td>
<td>1,4-dioxane</td>
<td>OMs</td>
<td>24</td>
<td>ZnCl$_2$ (3)</td>
<td>reflux</td>
<td>trace</td>
</tr>
</tbody>
</table>

$^a$ All reactions were carried out on a 1.0 mmol reaction scale of starting material 2 using 3 mL of ionic liquid. $^b$ Isolated yield. $^c$ 1.3 equiv of NaHCO$_3$ used as an acid scavenger. $^d$ 1,4-Dioxane (4.5 mL), 3 equiv Lewis acid were used.

Ultimately, the model compound, 2-(3-methanesulfonyloxypropoxy)naphthalene was used. The use of mesyl compound converted better yield (75%) than using bromo compound in [bmim][BF$_4$] (entry 3). Also mesyl compound did not give byproduct such as dealkylated product 3b. Next, it was performed a series of cyclizations utilizing a variety of ionic liquids (entry 4-8). The use of [bmim][OTf] gave the product in 71% yield for 24 h (entry...
4). As shown in entry 5, the use of [bmim][PF₆] proved to be the best optimize condition (150 °C, 24 h, 85%). When the use of [bmim][SbF₆] and [bmim][NTf₂], reaction time was almost same in 33h, 31h, however yield was higher [bmim][NTf₂] (71%) than [bmim][SbF₆] (51%) (entry 6, 7). It was also used another Lewis acid such as ZnCl₂ (entry 10-12). The use of ZnCl₂ as catalyst gave the cyclized product in 54% yield together with the chlorinated by-product (35%) (entry 10). The use of mesylate compound in presence of ZnCl₂ gave the cyclized product in 27% yield for 24 h together with the chlorinated by-product (56%) (entry 12). These reactions are competitive reaction between cyclization and chlorination. It was found that cyclized reaction enhances the reactivity and selectivity in ionic liquids.

Cyclization of Various Substrates.

Table 2 illustrates the cyclization of various primary halide, secondary compound and phenyl moiety compound under same reaction conditions described previously (Table1, entry 5). When alkyl halides are used, the general reactivity order of Friedel-Crafts alkylation is F > Cl > Br > I. Our result was found to have reverse behavior I > Br > Cl > F (entry 1~4). The use of fluoro compound did not give product for 48h (entry 1). Chloro compound also gave trace amount of desired product for 48 h (entry 2). When the use of bromo compound, the product was obtained in 75% yield for 48h (entry 3). As shown in entry 4, the use of iodo compound gave the product in 78% yield for 20h. It was expected the good result the use of tosyl compound. But, tosyl compound gave the product more less yield (71%, 20 h, entry 4) than mesyl compound (85%, 24 h). When the use of thiol compound instead of ether compound, the yield was very low, 9% (entry 6), and major product was isolated as a dimerized compound.
Table 2. Cyclization of Various Alkyl Halides in [bmim][PF₆].

<table>
<thead>
<tr>
<th>entry</th>
<th>compound</th>
<th>reaction time (h)</th>
<th>yield (%)</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Compound 1" /></td>
<td>48</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Compound 2" /></td>
<td>48</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Compound 3" /></td>
<td>48</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Compound 4" /></td>
<td>20</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="Compound 5" /></td>
<td>24</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><img src="image6" alt="Compound 6" /></td>
<td>48</td>
<td>9</td>
<td>19% dimer</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7" alt="Compound 7" /></td>
<td>18</td>
<td>70</td>
<td>trace elimination</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8" alt="Compound 8" /></td>
<td>7 days</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td><img src="image9" alt="Compound 9" /></td>
<td>48</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td><img src="image10" alt="Compound 10" /></td>
<td>48</td>
<td>65</td>
<td>15% 5-methoxychromane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50% 7-methoxychromane</td>
</tr>
<tr>
<td>11</td>
<td><img src="image11" alt="Compound 11" /></td>
<td>48</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td><img src="image12" alt="Compound 12" /></td>
<td>48</td>
<td>4</td>
<td></td>
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<td>13</td>
<td><img src="image13" alt="Compound 13" /></td>
<td>48</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

* Unless otherwise noted, all reactions were carried out under the same condition as entry 5 in Table 1. * Isolated yield.
The use of alkyl compound gave the cyclized product compound in 78% yield for 7 days (entry 8). The reaction of 2-(2-methanesulfonyloxyethoxy)naphthalene did not give the desired product at all, and the starting material was recovered (entry 9). It was compared the EDG, EWG substituted effect with compounds (entry 10, 11, 12, and 13). *m*-Methoxy aryl ethers gave two isomers such as 5-methoxychroman and 7-methoxychroman (entry 10). The use of *p*-methoxy compound gave the product in 16% yield (entry 11). When *p*-phenyl substituted compound was employed as a starting material, the desired product was formed in 4% yield (entry 12). The use of EWG substituted compound such as bromo substituted compound did not give a target compound (entry 13).
III. Conclusion

In summary, it has been described the facile Friedel-Crafts type cyclization of primary and secondary alkyl mesyl ether compound in the ionic liquids in the absence of acidic catalyst. The ionic liquid reaction system not only enhances the reactivity of aromatic alkyl ether mesylate in the absence of Lewis acid but also enhances the selectivity. Besides it has also been investigated the reactivity of various leaving group such as bromide, chloride, fluoride, iodide, and tosylate in [bmim][PF$_6$]. Further studies on applications with other type compound reactions in ionic liquids are under investigation.
IV. Experimental Section

Materials. $^1$H and $^{13}$C NMR spectra were recorded on a 400 MHz spectrometer, and chemical shifts were reported in $\delta$ units (ppm) relative to tetramethylsilane. TLC analysis was performed using glass plate with silica gel 60 F$_{254}$. Flash column chromatography was performed with 230-400 mesh silica gel. All other known compounds and all ionic liquids were commercially available.

Typical Procedure of the Cyclization. (Entry 5 in Table 1).

2-(3-Methanesulfonyloxypropoxy)naphthalene ($^1$, 280 mg, 1.0 mmol) in [bmim][PF$_6$] (3.0 mL) was stirred at 150 °C for 24 h. The reaction time was determined by checking TLC. The reaction product was extracted from ionic liquid phase with ethyl ether (7 mL $\times$ 5). The ether layer was evaporated under reduced pressure. The residue was purified by flash column chromatography (5% EtOAc/hexane) to obtain 156.4 mg (0.85 mmol, 85%) of 2,3-dihydro-1$^H$-naphtho[2,1-$b$]pyran ($^2$) as a white solid, mp 33-34 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.14-2.20 (m, 2H), 3.06 (t, $J$ = 6.4 Hz, 2H), 4.26 (t, $J$ = 5.2 Hz, 2H), 7.05 (d, $J$ = 4.0 Hz, 1H), 7.34 (t, $J$ = 7.4 Hz, 1H), 7.49 (t, $J$ = 7.4 Hz, 1H), 7.61 (d, $J$ = 4.0 Hz, 1H), 7.75-7.82 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.3, 22.3, 66.1, 113.8, 119.0, 121.8, 123.2, 126.3, 127.6, 128.4, 128.8, 133.2, 152.5. MS (EI) 184 (M$^+$), 156, 141, 128 (100), 115, 102. HRMS (EI) calcd for C$_{13}$H$_{12}$O (M$^+$) 184.0884, Found 184.0884.

1-Methyl-2,3-dihydro-1$^H$-naphtho[2,1-$b$]pyran (Entry 7 in Table 2). 2-(3-Iodobutoxy)naphthalene (326.2 mg, 1.0 mmol) in [bmim][PF$_6$] (3.0 mL) was stirred at 150 °C for 18 h; white solid (0.70 mmol, 70%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.51 (d, $J$ = 6.8 Hz, 3H), 1.85-1.90 (m, 1H), 2.25-2.34 (m, 1H), 3.54-
3.60 (m, 1H), 4.33-4.41 (m, 2H), 7.10 (d, J = 9.2 Hz, 1H), 7.37 (t, J = 6.8 Hz, 1H), 7.53 (t, J = 8.2 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 22.0, 24.4, 28.7, 61.5, 118.7, 119.1, 122.0, 122.8, 126.2, 127.9, 128.6, 129.2, 132.6, 151.3. MS (FAB) 198 (M$^+$, 100), 197, 183, 157. HRMS (EI) calcld for C$_{14}$H$_{14}$O (M$^+$) 199.1123 Found 198.1052.

1-(2-Naphthoxy)-3-butene (Entry 7 in Table 2). 2-(3-Iodobutoxy)naphthalene (326.2 mg, 1.0 mmol) in [bmim][PF$_6$] (3.0 mL) was stirred at 150 °C for 18 h; colorless oil (trace); $^1$H NMR (400 MHz, CDCl$_3$) δ 2.60-2.66 (m, 2H), 4.15 (t, J = 6.6 Hz, 2H), 5.13-5.25 (m, 2H), 5.92-6.02 (m, 1H), 7.14-7.18 (m, 2H), 7.32-7.46 (m, 2H), 7.72-7.78 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 33.6, 67.2, 106.6, 117.1, 119.0, 123.5, 126.3, 126.7, 127.6, 128.9, 29.34, 134.5, 134.5, 156.8. MS (EI) 195 (M$^+$), 144 (100), 127, 115. HRMS (EI) calcld for C$_{14}$H$_{14}$O (M$^+$) 198.1045, Found 198.1043.

2,3-Dihydro-1H-naphtho[2,1-b]thiopyran (Entry 6 in Table 2). 2-(3-Methanesulfonyloxy)propynaphthalene (296.4 mg, 1.0 mmol) in [bmim][PF$_6$] (3.0 mL) was stirred at 150 °C for 48 h; white solid (0.09 mmol, 9 %), mp 91-92 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.30-2.36 (m, 2H), 3.07-3.10 (m, 2H), 3.19 (t, J = 6.4 Hz, 2H), 7.17 (d, J = 4.0 Hz, 1H), 7.37-7.52 (m, 2H), 7.56 (d, J = 4.0 Hz, 1H), 7.75 (d, J = 4.0 Hz, 1H), 7.79 (d, J = 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 23.3, 24.8, 27.1, 121.5, 124.4, 125.9, 126.3, 126.4, 127.0, 128.6, 130.1, 131.2, 132.9. MS (EI) 200 (M$^+$, 100), 185, 171, 165. HRMS (EI) calcld for C$_{13}$H$_{12}$S (M$^+$) 200.0660, Found 200.0662.
2,2’-[1,3-Propanediylbis(thio)]bisnaphthalene (Entry 6 in Table 2). 2-(3-Methanesulfonyloxy)propynaphthalene (296.4 mg, 1.0 mmol) in [bmim][PF₆] (3.0 mL) was stirred at 150 °C for 48 h; white solid (0.19 mmol, 19 %), mp 101-102 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.03-2.10 (m, 2H), 3.18 (t, J = 7.2 Hz, 4H), 7.39-7.48 (m, 6H), 7.66-7.78 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 28.2, 32.2, 125.6, 126.5, 127.1, 127.3, 127.7, 128.4, 131.7, 133.4, 133.7. MS (EI) 360 (M⁺), 356, 201, 173, 155, 115 (100), 91. HRMS (EI) calcd for C₂₃H₂₀S₂ (M⁺) 360.1006, Found 360.1003.

1,2,3,4-Tetrahydrophenanthrene (Entry 8 in Table 2). 2-(4-Methanesulfonylbutyl)naphthalene (278.4 mg, 1.0 mmol) in [bmim][PF₆] (3.0 mL) was stirred at 150 °C for 7 days; white solid (0.71 mmol, 71 %), mp 34 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.86-2.02 (m, 4H), 2.93 (t, J = 6.2 Hz, 2H), 3.14 (t, J = 6.2 Hz, 2H), 7.22 (d, J = 4.2 Hz, 1H), 7.42-7.53 (m, 2H), 7.63 (d, J = 4.0 Hz, 1H), 7.81 (d, J = 4.0 Hz, 1H), 7.98 (d, J = 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 22.9, 23.2, 25.6, 30.4, 122.8, 124.7, 125.6, 125.7, 128.3, 128.4, 131.5, 132.0, 132.5, 134.3. MS (EI) 182 (M⁺, 100), 165, 154, 141. HRMS (EI) calcd for C₁₄H₁₄ (M⁺) 182.1096, Found 182.1009.

5-Methoxychroman (Entry 10 in Table 2). 3-(3-Methanesulfonyloxy-n-propoxy)anisole (260.3 mg, 1.0 mmol) in [bmim][PF₆] (3.0 mL) was stirred at 150 °C for 48 h; colorless oil (0.15 mmol, 15 %); ¹H NMR (400 MHz, CDCl₃) δ 1.96-2.02 (m, 2H), 2.66 (t, J = 6.6 Hz, 2H), 3.82 (s, 3H), 4.15 (t, J = 5.0 Hz, 2H), 6.42 (d, J = 4.0 Hz, 1H), 6.48 (d, J = 4.0 Hz, 1H), 7.06 (t, J = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 19.2, 21.8, 55.4, 66.0, 101.6, 109.5, 111.3, 126.7, 155.7, 157.9. MS (EI) 164 (M⁺, 100), 149, 136. HRMS (EI) calcd for C₁₀H₁₂O₂ (M⁺)
7-Methoxychroman (Entry 10 in Table 2). 3-(3-Methanesulfonyloxy-n-propoxy)anisole (260.3 mg, 1.0mmol) in [bmim][PF_6] (3.0 mL) was stirred at 150 °C for 48 h; colorless oil (0.50 mmol, 50); ¹H NMR (400 MHz, CDCl₃) δ 1.94-2.04 (m, 2H), 2.73 (t, J = 6.4 Hz, 2H), 3.76 (s, 3H), 4.17 (t, J = 5.2 Hz, 2H), 6.38 (s, 1H), 6.45 (d, J = 4.0 Hz, 1H), 6.94 (d, J = 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 22.4, 24.1, 55.2, 66.5, 101.4, 106.9, 114.3, 130.2, 155.5, 158.9. MS (EI) 164 (M⁺, 100), 163, 136, 108. HRMS (EI) calcd for C₁₀H₁₂O₂(M⁺) 164.0837, Found 164.0832.

6-Methoxychroman (Entry 11 in Table 2). 4-(3-Methanesulfonyloxy-n-propoxy)anisole (260.3 mg, 1.0mmol) in [bmim][PF_6] (3.0 mL) was stirred at 150 °C for 48 h; colorless oil (0.20 mmol, 20 %); ¹H NMR (400 MHz, CDCl₃) δ 1.96-2.02 (m, 2H), 2.78 (t, J = 6.6 Hz, 2H), 3.75 (s, 3H), 4.14 (t, J = 5.0 Hz, 2H), 6.59 (s, 1H), 6.66-6.74 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 22.4, 25.1, 55.6, 66.3, 113.2, 114.3, 117.2, 122.7, 148.9, 153.1. MS (EI) 164 (M⁺, 100), 149, 136, 108. HRMS (EI) calcd for C₁₀H₁₂O₂(M⁺) 164.0837, Found 164.0832.

6-Phenylchroman (Entry 12 in Table 2). 4-(3-Methanesulfonyloxy-n-propoxy)byphenyl (306.4 mg, 1.0mmol) in [bmim][PF_6] (3.0 mL) was stirred at 150 °C for 48 h; white solid (0.04 mmol, 4 %), mp 41-42 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.02-2.08 (m, 2H), 2.86 (t, J = 6.6 Hz, 2H), 4.23 (t, J = 5.0 Hz, 2H), 6.87 (d, J = 4.0 Hz, 1H), 7.28-7.35 (m, 3H), 7.41 (t, J = 7.6 Hz, 1H), 7.52-7.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 22.4, 25.0, 66.6, 117.0, 122.4, 126.0, 126.5, 126.7, 128.5, 128.6, 133.3, 141.0, 154.5; MS (EI) 210 (M⁺, 100), 182, 164, 154,
Starting Material for Table 1.

2-(3-Methanesulfonylpropoxy)naphthalene (1): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.26-2.32 (m, 2H), 2.99 (s, 3H), 4.21 (t, $J = 5.8$ Hz, 2H), 4.49 (t, $J = 6.0$ Hz, 2H), 7.13-7.15 (m, 2H), 7.34-7.47 (m, 2H), 7.73-7.79(m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 29.1, 37.2, 63.2, 66.8, 106.7, 118.6, 123.8, 126.5, 126.7, 127.6, 129.1, 129.5, 134.4, 156.4. MS (EI) 280 (M$^+$), 137, 115 (100), 79. HRMS (EI) calcd for C$_{14}$H$_{16}$O$_4$S(M$^+$) 280.0769, Found 280.0770.

Starting Material for Table 2.

2-(3-Fluoropropoxy)naphthalene (Entry 1 in table 2): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.14-2.39 (m, 2H), 4.24 (t, $J = 6.2$ Hz, 2H), 4.72 (dt, $J = 46.8$, 5.8 Hz, 2H), 7.16-7.22 (m, 2H), 7.34-7.53 (m, 2H), 7.76-7.83( m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 30.4 (d, $J = 20.1$ Hz), 63.6 (d, $J = 5.3$ Hz), 80.8 (d, $J = 163.9$ Hz), 106.8, 118.8, 123.7, 126.4, 126.7, 127.6, 129.1, 129.4, 134.6, 156.7. MS (EI) 204 (M$^+$), 144 (100), 115. HRMS (EI) calcd for C$_{13}$H$_{13}$FO(M$^+$) 204.0950 , Found 204.0932.

2-(3-Chloropropoxy)naphthalene (Entry 2 in table 2): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.28-2.34 (m, 2H), 3.80 (t, $J = 5.0$ Hz, 2H), 4.25 (t, $J = 5.8$ Hz, 2H), 7.13-7.16 (m, 2H), 7.32-7.46 (m, 2H), 7.72-7.80(m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 32.3, 41.6, 64.3, 106.8, 118.8, 123.7, 126.4, 126.7, 127.6, 129.0, 129.4, 134.5, 156.7. MS (EI) 220 (M$^+$), 114 (100), 115. HRMS (EI) calcd for C$_{13}$H$_{13}$OCl (M$^+$) 220.0655, Found 220.0667.
2-(3-Bromopropoxy)naphthalene (Entry 3 in table 2): $^1$H NMR (400 MHz, CDCl$_3$) δ 2.36-2.43 (m, 2H), 3.66 (t, $J = 6.4$ Hz, 2H), 4.26 (t, $J = 5.8$ Hz, 2H), 7.12-7.22 (m, 2H), 7.34-7.48 (m, 2H), 7.74-7.79 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 30.0, 32.3, 65.3, 106.8, 118.8, 123.7, 126.4, 126.7, 127.6, 129.0, 129.4, 134.5, 156.6. MS (EI) 264 (M$^+$), 266 (M$^+$), 144 (100), 115. HRMS (EI) calcd for C$_{13}$H$_{13}$O$_7$Br (M$^+$) 264.0150, Found 264.0151.

2-(3-Iodopropoxy)naphthalene (Entry 4 in table 2): $^1$H NMR (400 MHz, CDCl$_3$) δ 2.32-2.38 (m, 2H), 3.43 (t, $J = 6.6$ Hz, 2H), 4.16 (t, $J = 5.8$ Hz, 2H), 7.15-7.17 (m, 2H), 7.35-7.49 (m, 2H), 7.49-7.80 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 2.7, 32.8, 67.1, 106.6, 118.8, 123.6, 126.4, 126.7, 127.6, 128.9, 129.4, 134.4, 156.5. MS (EI) 313, 312 (M$^+$), 185, 184, 144, 115 (100). HRMS (EI) calcd for C$_{13}$H$_{13}$OI (M$^+$) 312.0011, Found 312.0006.

2-(3-Toluenesulfonyloxypropoxy)naphthalene (Entry 5 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) δ 2.14-2.20 (m, 2H), 2.24 (s, 3H), 4.04 (t, $J = 5.8$ Hz, 2H), 4.30 (t, $J = 6.0$ Hz, 2H), 6.95-7.00 (m, 2H), 7.16 (d, $J = 4.0$ Hz, 2H), 7.33-7.47 (m, 2H), 7.69-7.78 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.4, 28.7, 62.81, 67.0, 106.4, 118.6, 123.7, 126.4, 126.7, 127.6, 127.7, 128.9, 129.2, 129.7, 132.5, 134.4, 144.7, 156.3. MS (EI) 356 (M$^+$), 213 (100), 184, 155, 144, 129, 115, 91. HRMS (EI) calcd for C$_{20}$H$_{20}$O$_4$S (M$^+$) 356.1082, Found 356.1080

2-(3-Methanesulfonyloxy)propynaphthalene (Entry 6 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) δ 2.06-2.13 (m, 2H), 2.99 (s, 3H), 3.14 (t, $J = 6.8$ Hz, 2H), 4.38 (t, $J = 6.0$ Hz, 2H), 7.42-7.49 (m, 3H), 7.75-7.81 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 28.4, 29.5, 37.2, 68.0, 125.9, 126.7, 127.0, 127.5, 127.7, 128.6,
2-(3-Iodobutoxy)naphthalene (Entry 7 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.06 (d, $J = 6.8$ Hz, 3H), 2.13-2.36 (m, 2H), 4.14-4.27 (m, 2H), 4.48-4.53 (m, 1H), 7.15-7.19 (m, 2H), 7.35-7.49 (m, 2H), 7.76-7.81 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 25.6, 29.1, 41.9, 67.4, 106.6, 118.8, 123.6, 126.4, 126.7, 127.6, 128.9, 129.4, 134.4, 156.5. MS (EI) 326 (M$^+$), 199, 198, 157, 144 (100), 127, 11. HRMS (EI) calcd for C$_{14}$H$_{15}$OI (M$^+$) 326.0168, Found 326.0147.

2-(4-Methanesulfonylbutyl)naphthalene (Entry 8 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.78-1.89 (m, 4H), 2.83 (t, $J = 6.8$ Hz, 2H), 2.93 (s, 3H), 7.33 (d, $J = 4.0$ Hz, 1H), 7.41-7.49 (m, 2H), 7.62 (s, 1H), 7.78-7.83 (m, 3H) $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 27.0, 28.6, 35.3, 37.3, 69.8, 125.2, 126.0, 126.5, 127.1, 127.4, 127.6, 128.0, 132.0, 133.5, 139.0. MS (EI) 278 (M$^+$), 182, 167, 154, 141 (100). HRMS (EI) calcd for C$_{15}$H$_{18}$O$_3$S (M$^+$) 278.0977, Found 278.0972.

2-(2-Methanesulfonylethoxy)naphthalene (entry 9 in table 2): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.11 (s, 3H), 4.34-4.37 (m, 2H), 4.63-4.65 (m, 2H), 7.36-7.49 (m, 2H), 7.49-7.80 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 37.8, 65.7, 68.0, 106.8, 118.4, 124.1, 126.6, 126.8, 127.7, 129.2, 129.7, 134.3, 155.8. MS (EI) 266 (M$^+$), 144, 123 (100), 115, 79. HRMS (EI) calcd for C$_{13}$H$_{14}$O$_4$S (M$^+$) 266.0613, Found 266.0616.

3-(3-Methanesulfonyloxy- $n$-propoxy)anisole (Entry 10 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.19-2.25 (m, 2H), 2.99 (s, 3H), 3.79 (s, 3H), 4.07 (t, $J = 5.6$ Hz, 2H), 3.69-3.79 (m, 2H), 3.96-3.99 (m, 2H), 4.18-4.27 (m, 2H), 4.19-4.39 (m, 2H), 7.14-7.18 (m, 2H), 7.24-7.32 (m, 2H), 7.32-7.37 (m, 2H), 7.40-7.49 (m, 2H), 7.76-7.81 (m, 3H). MS (EI) 372 (M$^+$), 216, 145, 133 (100). HRMS (EI) calcd for C$_{15}$H$_{18}$O$_5$S (M$^+$) 372.1312, Found 372.1310.
Hz, 2H), 4.44 (t, J = 6.0 Hz, 2H), 6.45-6.54 (m, 3H), 7.18 (t, J = 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 29.0, 37.1, 55.2, 63.1, 66.7, 100.9, 106.5, 130.0, 159.6, 160.8. MS (EI) 260 (M$^+$), 164, 137 (100), 124, 95, 79. HRMS (EI) calcd for C$_{11}$H$_{16}$O$_5$S (M$^+$) 260.0718, Found 260.0720

4-(3-Methanesulfonyloxy-n-propoxy)anisole (Entry 11 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) δ 2.16-2.22 (m, 2H), 2.97 (s, 3H), 3.75 (s, 3H), 4.02 (t, J = 5.6 Hz, 2H), 4.43 (t, J = 6.0 Hz, 2H), 6.82 (s, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 29.0, 37.0, 55.6, 63.6, 66.8, 114.5, 115.3, 152.4, 153.9. MS (EI) 260 (M$^+$), 137 (100), 123, 109, 79. HRMS (EI) calcd for C$_{11}$H$_{16}$O$_5$S (M$^+$) 260.0717, Found 260.0717

4-(3-Methanesulfonyloxy-n-propoxy)byphenyl (Entry 12 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) δ 2.23-2.29 (m, 2H), 3.01 (s, 3H), 4.14 (t, J = 5.8 Hz, 2H), 4.48 (t, J = 6.2 Hz, 2H), 6.96-7.00 (m, 2H); 7.30-7.45 (m, 3H), 7.52-7.57 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 29.1, 37.2, 63.2, 66.7, 114.7, 126.7, 126.7, 128.2, 128.7, 134.1, 140.6, 158.0. MS (EI) 306 (M$^+$), 210, 170, 137 (100), 115. HRMS (EI) calcd for C$_{16}$H$_{18}$O$_4$S (M$^+$) 306.0926, Found 306.0929

1-Bromo-4-(3-Methanesulfonyloxypropoxy)benzene (Entry 13 in Table 2): $^1$H NMR (400 MHz, CDCl$_3$) δ 2.18-2.24 (m, 2H), 2.99 (s, 3H), 4.05 (t, J = 5.8 Hz, 2H), 4.43 (t, J = 6.2 Hz, 2H), 6.77 (d, J = 4.0 Hz, 2H), 7.37 (d, J = 4.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 29.0, 37.2, 63.4, 66.5, 113.2, 116.2, 132.3, 157.5. MS (EI) 310 (M$^+$), 308 (M$^+$), 174, 172, 137 (100), 109. HRMS (EI) calcd for C$_{10}$H$_{13}$O$_4$S$_{81}$Br (M$^+$) 309.9698, Found 309.9695
**Ionic Liquids Information**

All ionic liquids were spectrometrically pure and obtained from FutureChem. Co., Ltd. (www.futurechem.co.kr).

1-\textit{n}-Butyl-3-methylimidazolium tetrafluoroborate [bmim][BF$_4$]: water contents, 1,300 ppm; chloride, 50 ppm.

1-\textit{n}-Butyl-3-methylimidazolium hexafluorophosphate [bmim][PF$_6$]: water contents, 400 ppm; chloride, 30 ppm.

1-\textit{n}-Butyl-3-methylimidazolium hexafluoroantimonate [bmim][SbF$_6$]: water contents, 100 ppm; chloride, 30 ppm.

1-\textit{n}-Butyl-3-methylimidazolium triflate [bmim][OTf]: water contents, 400 ppm; chloride, 50 ppm.

1-\textit{n}-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [bmim][NTf$_2$]: water contents, 140 ppm; chloride, 30 ppm.
References


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NMR Spectrum (\(^1\)H and \(^{13}\)C NMR)

2,3-dihydro-\(^1\)H-naphtho[2,1-b]pyran \(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (100 MHz, CDCl\(_3\))
1- Methyl-2,3-dihydro-1H-naphtho[2,1-b]pyran $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(2-Naphthoxy)-3-butene \(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^1\)C NMR (100 MHz, CDCl\(_3\))
2,3-Dihydro-1H-naphtho[2,1-b]thiopyran $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,2’-[1,3-Propanediylbis(thio)]bisnaphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1,2,3,4-Tetrahydrophenanthrene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5-Methoxychroman \(^1\)H NMR (400 MHz, CDCl\(_3\))

\[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\))
7-Methoxychroman $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6-Methoxychroman $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6-Phenylchroman $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(3-Fluoropropoxy)naphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(3-Chloropropoxy)naphthalene

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(3-Bromopropoxy)naphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

35
2-(3-Iodopropoxy)naphthalene $^1$H NMR (400 MHz, CDCl₃)

$^{13}$C NMR (100 MHz, CDCl₃)
2-(3-Methylbenzensulfonylpropoxy)naphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(3-Methylsulfonylpropylthio)naphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(3-Iodobutoxy)naphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(4-Methanesulfonylbutyl)naphthalene

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(2-Methanesulfonyloxy)naphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-(3-Methanesulfonyloxy-n-propoxy)anisole $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(3-Methanesulfonyloxy-\textit{n}-propoxy)anisole $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(3-Methanesulfonyloxy-n-propoxy)byphenyl $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-Bromo-4-(3-Methanesulfonyloxypropoxy)benzene $^1$H NMR (400 MHz, CDCl$_3$)
Part II. Structural Modification of Polymer-Supported Ionic Liquids (PSIL): “Ionic Resins” as Catalysts for Nucleophilic Substitution Reactions
Abstract

Part II. Structural Modification of Polymer-Supported Ionic Liquids (PSIL): “Ionic Resins” as Catalysts for Nucleophilic Substitution Reactions

Nucleophilic fluorination reactions of some halo- and mesylalkanes to the corresponding fluoroalkanes with KF in the presence of ionic liquid ([bmim][BF₄]) under various reaction conditions were reported. New polystyrene based polymer-supported ionic liquid systems which called “ionic resin” as a high efficient catalyst for nucleophilic fluorination and substitutions were studied. The nucleophilic fluorination of 2-(3-methanesulfonyloxypropyl)naphthalene as a model compound with some alkali metal fluorides in the presence of 0.5 equiv of ionic liquid portion of ionic resin PS[alkylmim][BF₄] were completed within 0.8 - 6 h, affording the fluoroalkane (93-99%). The fluorination using PS[hmim][BF₄] as an immobilized catalyst proceeds much faster than that using the same amount of ionic liquid itself considered as the phase transfer catalytic system, as well as that using 18-crown-6. These ionic resins have the merits of significantly enhancement of the metal salts as nucleophiles compared with using ionic liquid itself.
요약문

Part II. 이온성 액체가 고정화된 고분자 화합물; 친핵성 치환 반응을 위한 촉매로서 이온성 수지.

이온성 액체가 플루오르화 반응을 포함하여 다양한 친핵성 치환 반응에 탁월한 반응성 증가의 효과가 있는 것을 발표하였다. 이러한 이온성 액체를 폴리스티렌을 골격으로 하는 고분자에 고정화 시킴으로써 "이온성 수지"라고 명명한 새로운 고분자 화합물을 합성하였고 이 이온성 수지는 불소화 반응을 포함하는 친핵성 치환 반응에 매우 효과적인 촉매임을 발견하였다. 이온성 액체 부분이 0.5 당량을 포함하는 이온성 수지 PS[alkylmim][BF₄]와 알킬 금속 플로라이드를 사용하는 2-(3-메탄올 포닐옥시프로필)나프탈렌의 친핵성 치환 반응은 0.8-6시간 안에 종결되어 플루오로알칸 (93-99%)을 얻을 수 있다. 고정화된 형태의 촉매인 PS[hmim][BF₄]를 사용하는 플루오르화 반응은 고정화 되지 않은 형태의 이온성 액체를 사용하는 반응보다 더 좋은 반응성을 보여주었다. 이는 18-crown-6과 상전이 촉매에서 이들 촉매가 고분자 지지체에 고정화되면 촉매 활성이 감소된다는 결과와 비교하면 획기적인 촉매라 할 수 있다.
I. Introduction

Although nucleophilic substitutions with metal salts as nucleophiles are crucial synthetic transformations, these reactions — especially, fluorinations — often proceed sluggishly because of the limited solubility and low nucleophilicity of metal salts in organic solvents. Phase transfer catalysts such as crown ethers and quaternary ammonium or phosphonium salts have been used to enhance the solubility and nucleophilicity of the metal salt in organic solvent systems, consequently accelerating the reaction rate. However, phase transfer catalysts are ineffective when the metal and nucleophile form a tight ion pair, and some quaternary ammonium salt catalysts are thermal unstable. There are many reports in which catalysts of this nature are immobilized — called triphase catalysts — to facilitate product isolation and enable catalyst recovery by simple filtration. However, nucleophilic displacements using such solid-supported phase transfer catalysts generally proceed at slower rates than those using the corresponding non-immobilized catalysts.

Due to their unique physical and chemical properties, ionic liquids containing imidazolium cations and their counter anions have currently received much attention as alternative reaction media for conducting various chemical processes. Recently, I reported highly efficient nucleophilic fluorination and other substitution reactions using alkali metal salts in the presence of ionic liquids. In these transformations, the ionic liquid not only significantly enhanced the reactivity of the alkali metal salts, but they also reduced by-product formation compared with the use of conventional protocols. However, I encountered problems when the product was polar and contained many heteroatoms, because it became difficult to extract it from the ionic liquid.
To overcome this drawback of ionic liquids, I have designed a polymer-supported ionic liquid (Figure 1) that can be used for nucleophilic displacements. There have been some recent efforts to prepare immobilized ionic liquids. Mehnert et al. reported an ionic liquid supported on the surface of silica gel. However, these workers still used a non-immobilized ionic liquid to carry out their reaction, and the silica framework is also unstable against fluoride, water and acid. Recently, I also reported a new polystyrene-based polymer-supported ionic liquid system, which I term an “ionic resin”, as a highly efficient catalyst for nucleophilic fluorination and for other nucleophilic substitution reactions. These ionic resins have the advantage of significantly enhancing the nucleophilicity of the metal salts compared with conventional methods. Furthermore these ionic resins can be reused many times without decomposition and loss of activity.

In this report, I wish to introduce the structural modified “ionic resins” to study their catalytic activity depending on their structure such as portion of linkage, loading level of ionic liquid portion and counter anions. To these purpose, I have prepared many PSILs with different linker length, loading level of ionic liquid portion and counter anions. I also measured the swelling constant of ionic resin and the reactivity was much concerned with swelling abilities of these ionic resins in each solvent.

![Diagram](image)

**Figure 1.** Polystyrene supported ionic liquids: ionic resins.
II. Results and Discussion

Synthesis of Ionic Resins.

The ionic resins PS[alkylmim][X]\textsuperscript{10} were prepared by the procedure shown in Scheme 1.

Synthesis of Various Linker Length PSIL

Merrifield resin\textsuperscript{11} (1% DVB, 3.2 mmol Cl/g) was reacted with HOCH\textsubscript{2}(CH\textsubscript{2})\textsubscript{n}CH\textsubscript{2}Cl (n=1, 4, 10) in the presence of NaH in THF to obtain resin 1. Polystyrene-supported 1-n-Alkyl-3-Methylimidazolium Chloride (PS[alkylmim][Cl]) was prepared by direct reaction of resin 1 and 1-methylimidazole at 90 °C for 3 days. Further treatment of PS[alkylmim][Cl] with either NaBF\textsubscript{4} in acetone for 48 h provides Polystyrene-supported 1-n-Methyl-3-methylimidazolium Tetrafluoroborate (PS[mim][BF\textsubscript{4}]) (3.0 mmol ionic liquid portion/g), Polystyrene-supported 1-n-Propyl-3-methylimidazolium Tetrafluoroborate (PS[pmim][BF\textsubscript{4}]) (2.4 mmol ionic liquid portion/g), Polystyrene-supported 1-n-Hexyl-3-methylimidazolium Tetrafluoroborate (PS[hmim][BF\textsubscript{4}]) (2.2 mmol ionic liquid portion/g), Polystyrene-supported 1-n-Dodecyl-3-methylimidazolium Tetrafluoroborate (PS[dmim][BF\textsubscript{4}]) (1.8 mmol ionic liquid portion/g). These ionic resins were analyzed by \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{19}F NMR (solid state), and by elemental analysis.

Synthesis of Various Counter Anion PSIL

Merrifield resin\textsuperscript{11} (1% DVB, 3.2 mmol Cl/g) was reacted with HOCH\textsubscript{2}(CH\textsubscript{2})\textsubscript{4}CH\textsubscript{2}Cl in the presence of NaH in THF to obtain resin 1. PS[hmim][Cl] was prepared by direct reaction of resin 1 and 1-methylimidazole at 90 °C for 3 days. Further treatment of PS[hmim][Cl] with either NaBF\textsubscript{4}, NaPF\textsubscript{6},
NaSbF$_6$, KOTf, and KOAc in acetone for 48 h provides PS[hmim][BF$_4$] (2.2 mmol ionic liquid portion/g), Polystyrene-supported 1-n-Hexyl-3-methyltrimidazolium Hexafluorophosphate (PS[hmim][PF$_6$]) (2.1 mmol ionic liquid portion/g), Polystyrene-supported 1-n-Hexyl-3-methyltrimidazolium Hexafluoroantimonate (PS[hmim][SbF$_6$]) (1.6 mmol ionic liquid portion/g), 1-n-Hexyl-3-methyltrimidazolium Triflate (PS[hmim][OTf]) (2.1 mmol ionic liquid portion/g), and 1-n-Hexyl-3-methyltrimidazolium Acetate (PS[hmim][OAc]) (2.1 mmol ionic liquid portion/g). These ionic resins were analyzed by $^1$H, $^{13}$C and $^{19}$F NMR (solid state), and by elemental analysis.

**Synthesis of Various Loading Level PSIL**

Merrifield resin$^{11}$ (1% DVB, 0.9–3.2 mmol Cl/g) was reacted with HOCH$_2$(CH$_2$)$_n$CH$_2$Cl in the presence of NaH in THF to obtain resin 1. PS[hmim][Cl] was prepared by direct reaction of resin 1 and 1-methylimidazole at 90 °C for 3 days. Further treatment of PS[hmim][Cl] with either NaBF$_4$ in acetone for 48 h provides PS[hmim][BF$_4$] (2.2 mmol, 1.2 mmol, 0.9 mmol, and 0.6 mmol ionic liquid portion/g). These ionic resins were analyzed by $^1$H, $^{13}$C and $^{19}$F NMR (solid state), and by elemental analysis.

**Scheme 1.** Preparation of Polymer-supported Ionic Liquids: Ionic Resins

[Diagram of the synthesis process shown here]
Nucleophilic Substitution with Various Length of Linker of Ionic Resins.

Table 1. Nucleophilic Substitution of Mesylate with MX Using PS[alkylmim][BF₄] of Various Linker Length as a Catalyst.⁹

<table>
<thead>
<tr>
<th>entry</th>
<th>ionic resin</th>
<th>MX</th>
<th>time(h)</th>
<th>yield of product (%)ᵇ</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PS[mmim][BF₄]</td>
<td>CsF</td>
<td>6.0</td>
<td>93</td>
<td>trace alcohol</td>
</tr>
<tr>
<td>2</td>
<td>PS[pmim][BF₄]</td>
<td>CsF</td>
<td>3.5</td>
<td>95</td>
<td>trace alcohol</td>
</tr>
<tr>
<td>3</td>
<td>PS[hmim][BF₄]</td>
<td>CsF</td>
<td>3.0</td>
<td>97</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>PS[domim][BF₄]</td>
<td>CsF</td>
<td>2.5</td>
<td>96</td>
<td>trace alkene</td>
</tr>
<tr>
<td>5</td>
<td>PS[mmim][BF₄]</td>
<td>KBr</td>
<td>1.5</td>
<td>97</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>PS[pmim][BF₄]</td>
<td>KBr</td>
<td>1.0</td>
<td>97</td>
<td>trace SM</td>
</tr>
<tr>
<td>7</td>
<td>PS[hmim][BF₄]</td>
<td>KBr</td>
<td>1.0</td>
<td>99</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>PS[domim][BF₄]</td>
<td>KBr</td>
<td>0.8</td>
<td>99</td>
<td>-</td>
</tr>
</tbody>
</table>

ᵃ All reactions were carried out on a 1.0 mmol reaction scale of mesylate using 3 mmol of MX at 100 °C and equiv tells the mole of ionic liquid portion, not ionic resin.
ᵇ Isolated yield.

Table 1 illustrates nucleophilic substitution of 2-(3-methanesulfonyloxypropyl)naphthalene, as a model compound, with CsF or KBr in the presence of my various linker length ionic resins. When using PS[domim][BF₄] among the PS[mmim][BF₄], PS[pmim][BF₄], PS[hmim][BF₄], and PS[domim][BF₄], both the nucleophilic fluorination and bromination reaction proceed most quickly. This result means that the ionic resins which have the longer linker show the better catalytic activity for nucleophilic substitutions including fluorination.
Nucleophilic Substitution of Various Counter Anion as a Catalyst

As shown in Table 2, the nucleophilic substitutions – fluorination and acetylation reaction - with CsF or KOAc with various counter anion in the presence of 0.5 equiv of PS[hmim][X] (X = BF₄, PF₆, SbF₆, OTf). Entries 1, 2, 3 and 4 show that the fluorination of mesylate proceed nearly quantitatively (in 92 and 97% yields, respectively). Ionic resin that has tetrafluoroborate (BF₄⁻) as a its counter anion shows the best catalytic activity in the nucleophilic fluorination as shown entry 1.

I also carried out nucleophilic acetylation with various counter anion in the presence of 0.5 equiv of PS[hmim][X] (X = PF₆, SbF₆, OTf, OAc). Entries 5, 6, 7 and 8 show that the acetylation of bromo proceed nearly quantitatively (in 99% yields, respectively).
Table 2. Nucleophilic Substitution of Mesylate or Bromo with MX Using PS[hmim][X] of Various Counter Anion as a Catalyst.\textsuperscript{a}

\[
\begin{array}{cccccc}
\text{entry} & \text{Y} & \text{X} & \text{MX} & \text{time (h)} & \text{yield (%)}^b & \text{comments} \\
1 & \text{OMs} & \text{BF}_4^- & \text{CsF} & 3.0 & 97 & - \\
2 & \text{OMs} & \text{PF}_6^- & \text{CsF} & 5.0 & 94 & \text{trace alcohol} \\
3 & \text{OMs} & \text{SbF}_6^- & \text{CsF} & 4.5 & 96 & - \\
4 & \text{OMs} & \text{OTf}^- & \text{CsF} & 6.0 & 92 & 5\% \text{ alcohol} \\
5 & \text{Br} & \text{PF}_6^- & \text{KOA} & 5.5 & 99 & - \\
6 & \text{Br} & \text{SbF}_6^- & \text{KOA} & 2.5 & 99 & - \\
7 & \text{Br} & \text{OTf}^- & \text{KOA} & 4.0 & 99 & - \\
8 & \text{Br} & \text{OAc}^- & \text{KOA} & 1.5 & 99 & - \\
\end{array}
\]

\textsuperscript{a} All reactions were carried out on a 1.0 mmol reaction scale of mesylate or bromo using 3 mmol of MX at 100 °C and equiv tells the mole of ionic liquid portion, not PS[hmim][X]. \textsuperscript{b} Isolated yield.
Nucleophilic Substitutions Using Various Loading Level PS[hmim][BF$_4$] as a Catalyst.

**Table 3.** Nucleophilic Substitution of Mesylate with MX Using Various Loading Level PS[hmim][BF$_4$] as a Catalyst.$^a$

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>loading level (mmol/g)</th>
<th>CH$_3$CN (mL)</th>
<th>MX</th>
<th>time (h)</th>
<th>yield (%)$^b$</th>
<th>SM</th>
<th>TM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.2</td>
<td>2.5</td>
<td>CsF</td>
<td>3.0</td>
<td>-</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>7.5</td>
<td>CsF</td>
<td>4.5</td>
<td>-</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.2</td>
<td>10.0</td>
<td>CsF</td>
<td>4.5</td>
<td>5</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>10.0</td>
<td>CsF</td>
<td>4.5</td>
<td>16</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>10.0</td>
<td>CsF</td>
<td>4.5</td>
<td>17</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>10.0</td>
<td>CsF</td>
<td>4.5</td>
<td>29</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0$^c$</td>
<td>10.0</td>
<td>CsF</td>
<td>4.5</td>
<td>79</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.2</td>
<td>10.0</td>
<td>KBr</td>
<td>110 (min)</td>
<td>-</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.2</td>
<td>10.0</td>
<td>KBr</td>
<td>90 (min)</td>
<td>-</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.9</td>
<td>10.0</td>
<td>KBr</td>
<td>90 (min)</td>
<td>trace</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.6</td>
<td>10.0</td>
<td>KBr</td>
<td>80 (min)</td>
<td>-</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0$^c$</td>
<td>10.0</td>
<td>KBr</td>
<td>1.0</td>
<td>80</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All reactions were carried out on a 1.0 mmol reaction scale of mesylate using 3 mmol of MX at 100 °C and equiv tells the mole of ionic liquid portion, not PS[hmim][X]. $^b$ Isolated yield. $^c$ 500 mg of Polystyrene was used.
Table 3 illustrated the nucleophilic substitutions – fluorination and bromination reaction - with CsF or KBr in the presence of 0.5 equiv of various loading level (2.2, 1.2, 0.9, and 0.6 mmol/g) at PS[hmim][BF₄]. Whereas the fluorination using CsF in the presence of the higher loading level (2.2 mmol/g) PS[hmim][BF₄] show the faster reaction rate in the reaction, the nucleophilic bromination using KBr in the presence of the lower loading level (0.6 mmol/g) PS[hmim][BF₄] show the faster reaction rate in the reaction. It means that the fluorination reaction is enhanced by PSIL through only matrix effect, while the bromination reaction is enhanced by PSIL through both matrix effect and site isolated effect.

**Swelling Constant of Ionic Resin; PSIL (mL/g)**

I measured the swelling constant of ionic resin in each solvent as shown Table 4 to show the unique physical property of these ionic resins. Interestingly, these ionics resin have so good swelling constant in polar aprotic solvents such as acetonitrile, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).
Table 4. Swelling Constant of Ionic Resin; PSIL (mL/g) \(^a\)

<table>
<thead>
<tr>
<th>solvent</th>
<th>Merrifield resin</th>
<th>PS[hmim][Cl]</th>
<th>PS[hmim][BF4]</th>
<th>PS[hmim][OTf]</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>6.2 (6.4)(^b)</td>
<td>4.3</td>
<td>4.4</td>
<td>4.7</td>
</tr>
<tr>
<td>acetone</td>
<td>2.6</td>
<td>3.0</td>
<td>4.7</td>
<td>4.6</td>
</tr>
<tr>
<td>H(_2)O/acetone</td>
<td>1.8</td>
<td>3.6</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>benzene</td>
<td>6.0 (6.6)(^b)</td>
<td>4.0</td>
<td>3.6</td>
<td>4.0</td>
</tr>
<tr>
<td>CH(_3)CN</td>
<td>1.7</td>
<td>2.7</td>
<td>5.2</td>
<td>4.1</td>
</tr>
<tr>
<td>DMF</td>
<td>4.6 (4.8)(^b)</td>
<td>6.0</td>
<td>7.2</td>
<td>6.9</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>5.8 (6.0)(^b)</td>
<td>3.9</td>
<td>3.7</td>
<td>4.1</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>5.9 (6.0)(^b)</td>
<td>6.2</td>
<td>5.5</td>
<td>5.9</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>1.8</td>
<td>4.0</td>
<td>1.9</td>
<td>2.7</td>
</tr>
<tr>
<td>DMSO</td>
<td>1.7</td>
<td>5.6</td>
<td>6.5</td>
<td>6.2</td>
</tr>
</tbody>
</table>

\(^a\) Volumes were measured in syringes equipped with a sintered frit after equilibrating for 1 h using 100 mg of PS[hmim][X] (X = Cl, BF4, OTf). \(^b\) ref.

Nucleophilic Substitutions Using PS[hmim][BF\(_4\)] in Various Solvents

As shown in Table 5, the nucleophilic substitutions – fluorination and acetylation reaction - with CsF or KOAc with various solvent in the presence of 0.5 equiv of PS[hmim][BF\(_4\)]. Although the fluorination in DMF shows the best reaction rate, this reaction gave 21% of alcohol byproduct. The fluorination of mesylate 3a in acetonitrile proceeds nearly quantitatively, affording the fluoroalkane product in 96% yield (entry 1). Therefore, acetonitrile is the proper solvent for this reaction. I also carried out nucleophilic acetylation with various solvents in the presence of 0.5 equiv of PS[hmim][BF\(_4\)]. Entry 5 and 8 show that the acetylation of bromo proceed nearly quantitatively (in 99% yields, respectively).
Table 5. Nucleophilic Substitutions of Mesylate or Bromo 2 with CsF Using PS[hmim][BF₄] in Various Solvents.\textsuperscript{a}

![Chemical structure](attachment:image.png)

<table>
<thead>
<tr>
<th>entry</th>
<th>Y</th>
<th>MX</th>
<th>solvent</th>
<th>time (h)</th>
<th>yield of product (%)\textsuperscript{f}</th>
<th>2</th>
<th>3α</th>
<th>3β</th>
<th>3c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OMs</td>
<td>CsF</td>
<td>CH₃CN</td>
<td>3.0</td>
<td>-</td>
<td>96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>OMs</td>
<td>CsF</td>
<td>DMF</td>
<td>1.5</td>
<td>-</td>
<td>68</td>
<td>21</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OMs</td>
<td>CsF</td>
<td>1,4-dioxane</td>
<td>6.0</td>
<td>-</td>
<td>74</td>
<td>17</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>OMs</td>
<td>CsF</td>
<td>benzene</td>
<td>6.0</td>
<td>19</td>
<td>65</td>
<td>trace</td>
<td></td>
<td>5c</td>
</tr>
<tr>
<td>5</td>
<td>Br</td>
<td>KOAc</td>
<td>DMF</td>
<td>0.25</td>
<td>-</td>
<td>99</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Br</td>
<td>KOAc</td>
<td>CH₃CN</td>
<td>1.5</td>
<td>-</td>
<td>94</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Br</td>
<td>KOAc</td>
<td>1,4-Dioxane</td>
<td>6</td>
<td>-</td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Br</td>
<td>KOAc</td>
<td>benzene</td>
<td>14</td>
<td>-</td>
<td>99</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All reactions were carried out on a 1.0 mmol reaction scale of mesylate or bromo 2 using 3 mmol of MX at 100 °C and equiv tells the mole of ionic liquid portion, not PS[hmim][BF₄]. \textsuperscript{b} Isolated yield. \textsuperscript{c} NMR determined.
III. Conclusion

I wish to introduce the structural modified “ionic resins” that acts as a high efficient catalyst for nucleophilic fluorination and other substitutions, converting various halo- and sulfonyloxy-alkanes to the corresponding products to study their catalytic activity depending on their structure such as portion of linkage, loading level of ionic liquid portion and counter anions. The ionic resins which have the longer linker show the better catalytic activity for nucleophilic sunstitutions including fluorination. Ionic resin that has tetrafluoroborate ($\text{BF}_4^-$) as a its counter anion shows the best catalytic activity in both the nucleophilic fluorination and bromination. Ionic resins that the higher loading level of ionic portion show better catalytic activity in the fluorination. – by only matrix effect, while those that the lower loading level of ionic portion show good catalytic activity in the bromination. – by both matrix effect and site isolation effect. Ionics resin have so good swelling constant in polar aprotic solvents

The ionic resin itself has many practical merits: product recovery and purification is simple and catalyst recovery and reuse is practical, a technically attractive situation for the use of these materials in industrial chemical processing.
IV. Experimental Section

Materials. $^1$H and $^{13}$C NMR spectra were recorded on a 400 MHz spectrometer at room temperature, and chemical shifts were reported in $\delta$ units (ppm) relative to tetramethylsilane. Solid-state $^1$H, $^{13}$C and $^{19}$F NMR spectra were also recorded on 600 MHz spectrometer at room temperature. TLC analysis was performed using glass plate with silica gel 60 F$_{254}$. Flash chromatography was performed with 230-400 mesh silica gel. All other known compounds including ionic liquid were commercially available.

Typical Procedure.

1. Preparation and characterization of Polystyrene-supported ionic liquid: ionic resin.

Synthesis of Resin 1: 6-Chloro-1-hexanol (24.6 g, 180 mmol, 8 equiv) was added to a suspension of NaH (60% in mineral oil, 7.2 g, 180 mmol, 8 equiv) in dried THF at 0°C, and the mixture was stirred for 30 min at 0°C. 5.0 g (22.5 mmol, 1.0 equiv) of Merrifield peptide resin (1% DVB, 4.5 mmol Cl/g) was then added to the reaction mixture followed by tetra-$n$-butylammonium iodide (8.3 g, 22.5 mmol, 1.0 equiv), and the reaction mixture was stirred over 2 day at 25°C. After filtration, the resin was washed successively with THF, 1 N HCl, water, acetone-water (1:1), acetone, water, methanol, methylene chloride and finally diethyl ether. After drying under high vacuum 7.1 g of resin 1 was obtained and identified by solid state NMR and elemental analysis. Anal. Cl, 11.4 (3.2 mmol Cl/g); N, none. $^{13}$C NMR (solid state) $\delta$ 27-34 (C2-C5), 41 (aliphatic polystyrene skeleton), 46 (C1), 72 (O-benzyl position, C6), 129-146 (aromatic polystyrene skeleton).
Polystyrene-supported 1-n-Hexyl-3-methylimidazolium Chloride (PS[hmim][Cl]). Resin 1 (3.2 mmol Cl/g; 6.5 g, 20.8 mmol) in 1-methylimidazole (300 mL) stirred over 3 days at 90 °C and after which time it was cooled at 25 °C. After filtration, the resin was washed successively with methylene chloride, methanol, acetone-water (1:1), water, acetone-water (1:1), methanol, methylene chloride, acetone, and finally diethyl ether. After drying under high vacuum 7.8 g of PS[hmim][Cl] was obtained and identified by solid state NMR and elemental analysis. Anal. N, 7.1 (2.5 mmol ionic liquid portion/g); Cl, 8.1.

$^{13}$C NMR (solid state) δ 27-31 (C2’-C5’), 38 (N-CH$_3$), 41 (aliphatic polystyrene skeleton), 50 (C1’), 73 (O-benzyl position, C6’), 130 (C4, C5, aromatic polystyrene skeleton), 138 (C2), 146 (aromatic polystyrene skeleton).
Polystyrene-supported 1-n-Hexyl-3-methylimidazolium Tetrafluoroborate (PS[hmim][BF₄]). NaBF₄ (15.8 g, 144 mmol, 8 equiv) was added to the PS[hmim][Cl] (2.5 mmol ionic liquid portion/g; 7.2 g, 18.0 mmol, 1 equiv) in acetone (250 mL) and the mixture was stirred over 2 days at 25 °C. After filtration, the resin was wash repeatedly with acetone, acetone-water (1:1), water, acetone-water (1:1), acetone, and finally diethyl ether. After drying under high vacuum, 8.1 g of PS[hmim][BF₄] was obtained and identified by solid state NMR and elemental analysis. Anal. N, 6.2 (2.2 mmol ionic liquid portion/g); Cl, 0.1

$^{13}$C NMR (solid state) δ 27-31 (C₂’-C₅’), 37 (N-CH₃), 41 (aliphatic polystyrene skeleton), 50 (C₁’), 72 (O-benzyl position, C₆’), 128 (C₄, C₅, aromatic polystyrene skeleton), 137 (C₂), 146 (aromatic polystyrene skeleton); $^{19}$F NMR (solid state) δ –148. Considering $^{13}$C NMR data of ionic liquid [bmim][BF₄], $^{13}$C NMR (solid state) data of PS[hmim][BF₄] were assigned.
I prepared the following PSIL with same method above mentioned.

**Polystyrene-supported 1-Hexyl-3-methylimidazolium Tetrafluoroborate**

(PS[hmim][BF₄]): Anal. N, 3.3 (1.2 mmol ionic liquid portion/g); Cl, 0.2

**Polystyrene-supported 1-Hexyl-3-methylimidazolium Tetrafluoroborate**

(PS[hmim][BF₄]): Anal. N, 2.4 (0.9 mmol ionic liquid portion/g); Cl, 0.1

**Polystyrene-supported 1-Hexyl-3-methylimidazolium Tetrafluoroborate**

(PS[hmim][BF₄]): Anal. N, 1.7 (0.6 mmol ionic liquid portion/g); Cl, 0.1

**Polystyrene-supported 1-Methyl-3-methylimidazolium Tetrafluoroborate**

(PS[mmim][BF₄]): Anal. N, 8.3 (3.0 mmol ionic liquid portion/g); Cl, 0.2

**Polystyrene-supported 1-\(n\)-Propyl-3-methylimidazolium Tetrafluoroborate**

(PS[pmim][BF₄]): Anal. N, 6.4 (2.3 mmol ionic liquid portion/g); Cl, 0.1
Polystyrene-supported 1-\textit{n}-Dodecyl-3-methylimidazolium Tetrafluoroborate (PS[domim][BF\(_4\)]): Anal. N, 5.1 (1.8 mmol ionic liquid portion/g); Cl, 0.1

1-\textit{n}-Butyl-3-methylimidazolium Tetrafluoroborate ([bmim][BF\(_4\)]): \(^{13}\)C NMR (DMSO-\textit{d}\(_6\), 150 MHz) \(\delta\) 13.85 (C4'), 19.39, 31.97, 36.31 (N-CH\(_3\)), 49.15 (C1'), 122.86, 124.212, 137.09 (C2).

Polystyrene-supported 1-\textit{n}-Hexyl-3-methylimidazolium Triflate (PS[hmim][OTf]). KOTf (11.3 g, 60.0 mmol, 8 equiv) was added to the PS[hmim][Cl] (2.5 mmol ionic liquid portion/g; 3.0 g, 7.5 mmol, 1 equiv) in acetone (120 mL) and the mixture was stirred over 2 days at 25 °C. After filtration, the resin was wash repeatedly with acetone, acetone-water (1:1), water, acetone-water (1:1), acetone, methylene chloride and finally diethyl ether. After drying under high vacuum, 3.7 g of PS[hmim][OTf] was obtained and identified by solid state NMR and elemental analysis. Anal. N, 5.8 (2.1 mmol ionic liquid portion/g); Cl, < 0.2

\(^{13}\)C NMR (solid state) \(\delta\) 27-31 (C2'-C5'), 37 (N-CH\(_3\)), 41 (aliphatic polystyrene skeleton), 52 (C1'), 72 (O-benzyl position, C6'), 129 (C4, C5, aromatic polystyrene skeleton), 138 (C2), 147 (aromatic polystyrene skeleton); \(^{19}\)F NMR (solid state) \(\delta\) –77.
I prepared the followed PSIL with same method above mentioned.

**Polystyrene-supported 1-\textit{n}-Hexyl-3-methylimidazolium Hexafluorophosphate (PS[hmim][PF_6]).** Anal. N, 5.8 (2.1 mmol ionic liquid portion/g); Cl, 0.2

**Polystyrene-supported 1-\textit{n}-Hexyl-3-methylimidazolium Hexafluoroantimonate (PS[hmim][SbF_6]).** Anal. N, 4.4 (1.6 mmol ionic liquid portion/g); Cl, 0.2

**Polystyrene-supported 1-\textit{n}-Hexyl-3-methylimidazolium Acetate; PS[hmim][OAc].** Anal. N, 5.9 (2.1 mmol ionic liquid portion/g); Cl, 0.2
References


(10) Polystyrene-supported 1-\(n\)-hexyl-3-methylimidazolium cation PS[hmim] and its counter anions: tetrafluoroborate \([\text{BF}_4]\), triflate \([\text{OTf}]\) are used.