

# Synthesis of Polyoxymethylene Dimethyl Ethers Catalyzed by Brønsted Acid Ionic Liquids with Alkanesulfonic Acid Groups

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**ABSTRACT:** Catalytic reaction of methylal (DMM) with trioxane (TOX) for preparation of polyoxymethylene dimethyl ethers (PODME<sub>n</sub>, CH<sub>3</sub>O(CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub>, where  $n > 1$ ) was investigated in a series of Brønsted acid ionic liquids with alkanesulfonic acid groups. The structures, acidities, and properties of ionic liquids were experimentally characterized and theoretically analyzed. The Brønsted acidity–activity correlation for the ionic liquids was studied. Among all these ionic liquids, 1-(4-sulfonic acid) butylpyridinium hydrogen sulfate ([PY-BS][HSO<sub>4</sub><sup>−</sup>]) exhibited the best catalytic performance, which was ascribed to its strong Brønsted acidity. The influences of ionic liquid dosage, molar ratio of DMM to TOX, and reaction temperature on the catalytic reaction were explored using [PY-BS][HSO<sub>4</sub><sup>−</sup>] as the catalyst. Under the optimal conditions of  $n(\text{methylal}):n(\text{trioxane}):n(\text{ILs}) = 180:60:1$ , 170 °C, and 10h, the conversion of trioxane and the selectivity of PODME<sub>3–8</sub> were as high as 91.18% and 70.90%, respectively. The ionic liquid [PY-BS][HSO<sub>4</sub><sup>−</sup>] could be reused.

## 1. INTRODUCTION

With the shortage and unsustainable consumption of crude oil, diesel often experiences short supply.<sup>1–3</sup> Diesel components have high molecular weight, low combustion efficiency, and serious environmental issues. Therefore, it is increasingly necessary to develop synthesis of oxygenated compounds (molecules which contain oxygen in their structures) as diesel additives to alleviate the diesel supply crisis and environmental pollution.<sup>4</sup> Polyoxymethylene dimethyl ethers (PODME<sub>n</sub>) are novel oxygenated compounds with the formula CH<sub>3</sub>O-(CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub>, where  $n \geq 1$ , and they can be used as promising green diesel additives with high oxygen content (42%–51%), high cetane number, reducing pollutants, and without changing the engine infrastructure.<sup>4–9</sup> PODME <sub>$n=1,2$</sub>  show low flash point and boiling point. PODME <sub>$n>8$</sub>  show the risk of precipitate at low temperatures.<sup>10</sup> Considering the influences of vapor pressure, boiling point, and solubility in diesel, PODME<sub>3–8</sub> are ideal diesel additives among PODME <sub>$n$</sub> .<sup>11</sup> Zhao et al. found that the NO<sub>x</sub> and emissions of particulate pollutants could be reduced significantly by adding 10%–20% PODME<sub>3–8</sub> to diesel.<sup>6</sup>

PODME <sub>$n$</sub>  is usually produced by the end-group (–CH<sub>3</sub>) provider and the chain-group (–CH<sub>2</sub>O–) provider with the existence of catalysts. Generally, the former contains methanol, methylal, or dimethyl ether and the latter contains trioxane, formaldehyde, or paraformaldehyde.<sup>6–11</sup> Patrini et al. used CF<sub>3</sub>SO<sub>3</sub>H as the catalyst to prepare PODME <sub>$n$</sub>  with methylal and paraformaldehyde as starting materials.<sup>12</sup> However, the strong acid is corrosive and environmentally unfriendly, which limits the application of liquid catalysts. Arvidson et al. prepared PODME <sub>$n$</sub>  by the reaction of trioxane, methylal, and paraformaldehyde using cation exchange resin as catalyst.<sup>13</sup> The disadvantages of this approach are the low yield of PODME<sub>2–4</sub> (33.0%) and easy deactivation of the catalyst. Therefore, the development of environmentally friendly and efficient catalysts for synthesis of PODME <sub>$n$</sub>  is extremely urgent.

In recent years, room-temperature ionic liquids, as environmentally benign and “designer” solvents or catalysts, have attracted much attention because of numerous advantages, such as wide liquid range, high catalytic activity, ignorable vapor pressure, designed structure, and easy separation from the reaction system.<sup>14–17</sup> Chen et al. prepared PODME <sub>$n$</sub>  from methanol and trioxane by employing ionic liquid as the catalyst.<sup>18</sup> However, the yield of PODME<sub>3–8</sub> was low for the reaction of methanol and trioxane.

In this work, a series of ionic liquids with alkanesulfonic acid groups were synthesized. They were characterized by infrared (IR) spectra, nuclear magnetic resonance (NMR), electrospray ionization mass spectrum (ESI-MS), and differential thermal analysis (TG-DTA). Their Brønsted acidity was determined through ultraviolet–visible (UV–vis) spectroscopy. Their catalytic performances for the synthesis of PODME <sub>$n$</sub>  from methylal (DMM) and trioxane (TOX) were investigated. A correlation between Brønsted acid strength of ionic liquids and catalytic activities was discussed. The effects of reaction conditions on the production in the selected ionic liquids were extensively studied.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Instruments.** Methylimidazole (99%) was purchased from Linhai Kaile Chemical Factory. 1,3-Propane sultone (99%) and 1,4-butane sultone (99%) were purchased from Wuhan Fengfan Chemical Co, Ltd. Pyridine, triethylamine, concentrated sulfuric acid, anhydrous methanol, acetone, and Toluene were purchased from Beijing Chemicals Factory. Methylal (99.8%) was purchased from Alfa Aesar-Johnson Matthey. Trioxane (99.8%) was purchased from

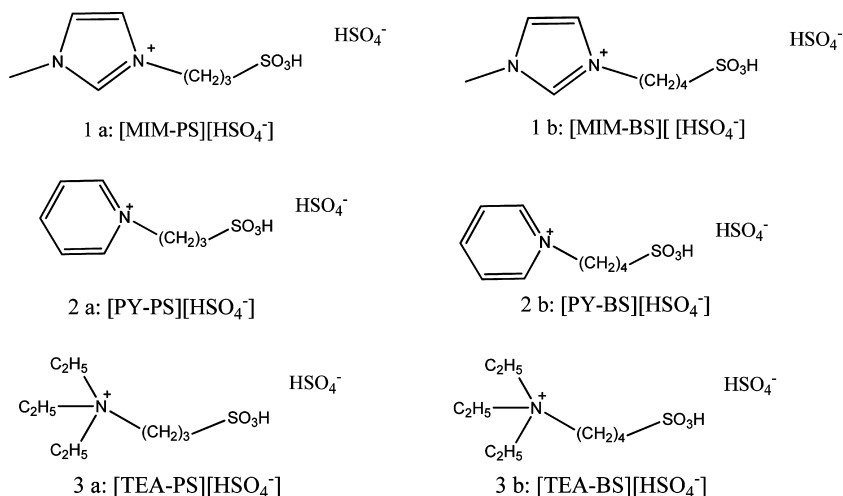
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Scheme 1. Structures of the Six Alkane Sulfonic Acid-Functionalized Ionic Liquids



Aladdin Reagent Co, Ltd. All the materials (analytical-reagent grade) were commercially available and used without further purification.

IR spectra were run on a PerkinElmer Spectrum, which used KBr windows suitable for Fourier transform infrared (FTIR) transmittance technology to form a liquid film. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a JEOL JNM-ECA600 nuclear magnetic resonance spectrometer. Chemical shifts are reported in parts per million (ppm,  $\delta$ ). ESI-MS spectra were measured on a Thermo Electron Corporation FINNIGAN LTQ instrument. Thermal decomposition temperature was determined by a PerkinElmer TGA7 TG-DTA instrument, with a heating rate of 10 °C/min from room temperature to 600 °C.

**2.2. Preparation of Alkanesulfonic Acid-functionalized Ionic Liquids.** The alkanesulfonic acid-functionalized ionic liquids were synthesized according to the literature,<sup>12,19,20</sup> and the structures of these ionic liquids are shown in Scheme 1.

A stoichiometric amount of 1,3-propane or 1,4-butane sultone was added dropwise to *N*-methylimidazole, pyridine, or triethylamine at room temperature without solvent. The mixture was stirred at 50 °C for 2 days. The formed white zwitterions, all of which are white solids, were centrifuged and washed three times with anhydrous ether to remove unreacted materials and then dried in a vacuum oven at 80 °C for 24 h. All of the white solids were freely soluble in water and did not dissolve in some organic solvents, such as toluene and acetone.

A stoichiometric amount of concentrated sulfuric acid was added dropwise to the zwitterions at room temperature. The mixture was stirred at 40–90 °C for 2–3 days until liquefied, resulting in the formation of the alkanesulfonic acid-functionalized ionic liquids. The ionic liquids were washed three times with toluene and anhydrous ether to remove unreacted materials and dried in a vacuum oven at 80 °C for 24 h.

The ionic liquids were fully characterized by FT-IR, NMR, ESI-MS, and TG-DTA, and the spectral data agreed with their structures.

**2.2.1. Spectral Data for [MIM-PS][HSO<sub>4</sub><sup>-</sup>].** IR (KBr, cm<sup>-1</sup>): 3149, 3108, 1578, 1453, 1237, 1168, 1050, 570. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 2.117 (m, 2H), 2.505 (t, 2H, *J* = 7.6 Hz), 3.857 (s, 3H), 4.306 (t, 2H, *J* = 7.2 Hz), 4.744 (s, 2H), 7.682 (s, 1H), 7.754 (s, 1H), 9.087 (s, 1H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 26.507, 36.251, 47.919, 48.247, 122.809, 124.137, 137.247. Positive-ion ESI-MS *m/z*: 205.06

(MIMPS<sup>+</sup>). Negative-ion ESI-MS *m/z*: 96.92 (HSO<sub>4</sub><sup>-</sup>). TG-DTA (N<sub>2</sub>, 10 °C/min): *T*<sub>d</sub>, 323 °C.

**2.2.2. Spectral Data for [MIM-BS][HSO<sub>4</sub><sup>-</sup>].** IR (KBr, cm<sup>-1</sup>): 3156, 3100, 1578, 1466, 1223, 1160, 1050, 576. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 1.540 (m, 2H), 1.877 (m, 2H), 2.497 (t, 2H, *J* = 7.6 Hz), 3.853 (s, 3H), 4.184 (t, 2H, *J* = 6.9 Hz), 7.707 (s, 1H), 7.773 (s, 1H), 8.226 (bs, 2H), 9.138 (s, 1H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 21.634, 28.537, 35.728, 48.510, 50.387, 122.312, 123.605, 136.559. Positive-ion ESI-MS *m/z*: 219.08 (MIMBS<sup>+</sup>). Negative-ion ESI-MS *m/z*: 96.94 (HSO<sub>4</sub><sup>-</sup>). TG-DTA (N<sub>2</sub>, 10 °C/min): *T*<sub>d</sub>, 324 °C.

**2.2.3. Spectral Data for [PY-PS][HSO<sub>4</sub><sup>-</sup>].** IR (KBr, cm<sup>-1</sup>): 3007, 2927, 1696, 1473, 1224, 1168, 1035, 597. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 2.242 (m, 2H), 2.468 (t, 2H, *J* = 6.8 Hz), 4.739 (t, 2H, *J* = 7.6 Hz), 7.705 (bs, 2H), 8.157 (t, 2H, *J* = 6.8 Hz), 8.603 (t, 1H, *J* = 8.8 Hz), 9.094 (d, 2H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 27.778, 47.540, 60.121, 128.609, 145.489, 146.016. Positive-ion ESI-MS *m/z*: 202.04 (PYPS<sup>+</sup>). Negative-ion ESI-MS *m/z*: 96.91 (HSO<sub>4</sub><sup>-</sup>). TG-DTA (N<sub>2</sub>, 10 °C/min): *T*<sub>d</sub>, 319 °C.

**2.2.4. Spectral Data for [PY-BS][HSO<sub>4</sub><sup>-</sup>].** IR (KBr, cm<sup>-1</sup>): 3073, 2927, 1627, 1487, 1216, 1174, 1050, 583. <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O,  $\delta$ ): 1.226 (m, 2H), 1.600 (m, 2H), 2.392 (t, 2H, *J* = 7.6 Hz), 4.085 (t, 2H, *J* = 6.9 Hz), 4.650 (s, 2H), 7.511 (t, 2H, *J* = 6.8 Hz), 7.982 (t, 1H, *J* = 8.4 Hz), 8.284 (d, 2H). <sup>13</sup>C NMR (150 MHz, D<sub>2</sub>O,  $\delta$ ): 20.778, 29.175, 49.905, 61.069, 128.236, 144.091, 145.624. Positive-ion ESI-MS *m/z*: 216.05 (PYBS<sup>+</sup>). Negative-ion ESI-MS *m/z*: 96.86 (HSO<sub>4</sub><sup>-</sup>). TG-DTA (N<sub>2</sub>, 10 °C/min): *T*<sub>d</sub>, 320 °C.

**2.2.5. Spectral Data for [TEA-PS][HSO<sub>4</sub><sup>-</sup>].** IR (KBr, cm<sup>-1</sup>): 2941, 1223, 1153, 1050, 570. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 1.189 (t, 9H, *J* = 6.8 Hz), 1.913 (m, 2H), 2.546 (t, 2H, *J* = 6.8 Hz), 3.221 (q, 6H), 3.325 (m, 2H), 3.885 (s, 2H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.559, 18.449, 47.881, 52.566, 55.687. Positive-ion ESI-MS *m/z*: 224.14 (TEAPS<sup>+</sup>). Negative-ion ESI-MS *m/z*: 96.90 (HSO<sub>4</sub><sup>-</sup>). TG-DTA (N<sub>2</sub>, 10 °C/min): *T*<sub>d</sub>, 317 °C.

**2.2.6. Spectral Data for [TEA-BS][HSO<sub>4</sub><sup>-</sup>].** IR (KBr, cm<sup>-1</sup>): 2920, 1230, 1160, 1042, 592. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 1.157 (t, 9H, *J* = 7.2 Hz), 1.663 (m, 4H), 2.599 (t, 2H, *J* = 7.6 Hz), 3.186 (m, 8H), 10.089 (s, 2H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.308, 20.103, 22.177, 50.390, 52.242, 56.027. Positive-ion ESI-MS *m/z*: 238.20 (TEABS<sup>+</sup>). Negative-ion ESI-

MS  $m/z$ : 97.00 ( $\text{HSO}_4^-$ ). TG-DTA ( $\text{N}_2$ , 10 °C/min):  $T_d$ , 318 °C.

### 2.3. Brønsted Acidity Analysis of the Ionic Liquids.

The Brønsted acid strengths of ionic liquids were determined using UV–vis spectroscopy.<sup>21</sup> A series of different concentration of ionic liquids solutions were prepared, using *p*-nitroaniline as an indicator, and then the Hammett function ( $H_0$ ) was calculated as follows:

$$H_0 = \text{p}K_a + \log([I]/[HI])$$

where  $\text{p}K_a$  is the electrolytic constant of *p*-nitroaniline ( $\text{p}K_a = 0.99$ ) and  $[I]$  and  $[HI]$  are percentage of unprotonated and protonated *p*-nitroaniline, respectively.

### 2.4. Synthesis and Analysis of Polyoxymethylene Dimethyl Ethers (PODME<sub>*n*</sub>) Catalyzed by Ionic Liquids.

The reaction of methylal with trioxane was carried out in a 50 mL Teflon-lined stainless-steel autoclave, equipped with thermostat and mechanical stirring. Methylal, trioxane, and ionic liquid catalyst with different molar ratios were quantitatively introduced into the reactor successively. The reaction was allowed to proceed for 2–10 h and kept at the desired temperature. After the reaction was completed, the mixture was cooled and kept at 0 °C for 0.5 h, and two phases were formed. The upper phase consisted of the produced PODME<sub>*n*</sub> and the unreacted materials, and the lower phase contained the ionic liquid catalyst. The lower phase was simply separated from the upper phase by decantation.

The upper solution was analyzed by a Shimadzu GC-2014 instrument equipped with a FID detector. A capillary column (DB-5MS, 30 m × 0.25 μm; id, 0.25 μm) was used. The internal standard compound was methanol. Analytical conditions were as follows: injection port temperature, 290 °C; FID temperature, 300 °C; oven temperature program, initially the temperature was held at 40 °C for 5 min, then ramped to 280 °C at a rate of 5 °C/min and held for 5 min; carrier gas, nitrogen of 0.4 MPa; reagent gases, air of 0.4 MPa, hydrogen of 0.3 MPa.

## 3. RESULTS AND DISCUSSION

### 3.1. Brønsted Acidity Analyses of the Ionic Liquids.

The Brønsted acid strengths of various ionic liquids are shown in Table 1. The Brønsted acid strength of the ionic liquids is in the sequence  $[\text{PY-BS}][\text{HSO}_4^-] > [\text{PY-PS}][\text{HSO}_4^-] > [\text{MIM-BS}][\text{HSO}_4^-] > [\text{MIM-PS}][\text{HSO}_4^-] > [\text{TEA-BS}][\text{HSO}_4^-] > [\text{TEA-PS}][\text{HSO}_4^-]$ .  $[\text{PY-BS}][\text{HSO}_4^-]$  shows the strongest Brønsted acidity. The Brønsted acid strength of the ionic liquids with different nitrogen groups is in the sequence of

pyridine > *N*-methylimidazole > triethylamine. The pyridine ring and imidazole ring withdraw electrons, while the ethyl group donates electrons. Therefore, the density of positive charge on the nitrogen of pyridine and imidazole is greater than that for triethylamine. It is easier for the pyridinium-based and imidazolium-based ionic liquids to dissociate  $\text{H}^+$  ion than for the triethylammonium-based ionic liquid, resulting in stronger Brønsted acidity. In comparison with pyridinium-based ionic liquids, the positive charge is dispersed for the imidazole because of the conjugative effect. Therefore, it is easier for the pyridinium-based ionic liquid to dissociate  $\text{H}^+$  ion, resulting in a stronger Brønsted acidity. The Brønsted acid strength of ionic liquids with the same nitrogen groups but different carbon chains is in the sequences of  $(\text{CH}_2)_4 > (\text{CH}_2)_3$ . For ionic liquids with the same nitrogen groups, ionic liquids with a longer carbon chain tend to dissociate  $\text{H}^+$  ion more easily, which gives rise to a stronger Brønsted acidity.<sup>12</sup>

### 3.2. Reaction of Methylal with Trioxane for Preparation of PODME<sub>*n*</sub>.

**3.2.1. Effect of Ionic Liquids with Different Cations.** The effect of ionic liquids with different cations on the catalytic reaction was studied (see Figure 1). Figure 1a displays that the conversions of Trioxane ( $X_{\text{TOX}}$ ) are all above 90% for the six ionic liquids, but the selectivity values of the PODME<sub>3–8</sub> are distinctly different. Among all the ionic liquids,  $[\text{PY-BS}][\text{HSO}_4^-]$  shows the best catalytic performance. The cation of the ionic liquid has a significant effect on its catalytic activity. The selectivity values of the PODME<sub>3–8</sub> of ionic liquids with different cations are in the sequence  $[\text{PY-BS}][\text{HSO}_4^-] > [\text{PY-PS}][\text{HSO}_4^-] > [\text{MIM-BS}][\text{HSO}_4^-] > [\text{MIM-PS}][\text{HSO}_4^-] > [\text{TEA-BS}][\text{HSO}_4^-] > [\text{TEA-PS}][\text{HSO}_4^-]$ . On the basis of the above discussion of the Brønsted acidity analysis of the ionic liquids (section 3.1), the catalytic activity of the ionic liquid is related to the Brønsted strength. A strong Brønsted acidity contributes to catalytic reaction of methylal with trioxane for preparation of PODME<sub>*n*</sub>.<sup>13</sup> In addition, as shown in Figure 1b, the selectivity of the PODME<sub>*n*</sub> decreases with the increase of polymerization degrees. The selectivity of PODME<sub>*n*</sub> is in the sequence of  $n = 2 > n = 3 > n = 4 > n = 5 > n = 6 > n = 7 > n = 8$ . Therefore, the reaction mechanism is reliable in Figure 2. First, trioxane is converted to formaldehyde over the acidic catalyst. Formaldehyde represents the monomer of the PODME oligomers and reacts with methylal (DMM) to produce PODME<sub>*n=2*</sub>. In general, PODME<sub>*n*</sub> may react with formaldehyde to obtain PODME<sub>*n+1*</sub>.<sup>5</sup>

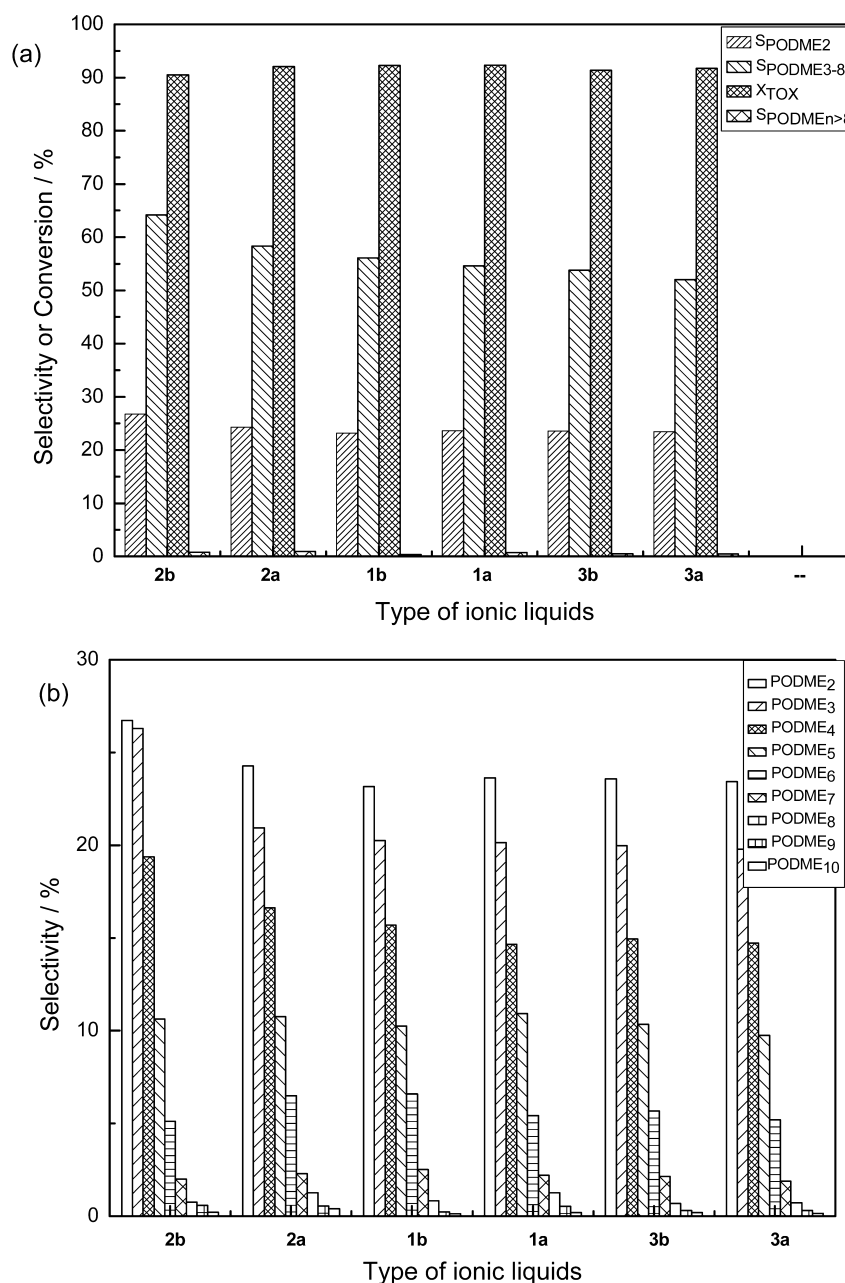
**3.2.2. Effect of Molar Ratio of Methylal to Trioxane.** A series of experiments were conducted using the best catalyst  $[\text{PY-BS}][\text{HSO}_4^-]$ . Figure 3 shows the effect of the molar ratio of methylal to trioxane on the catalytic reaction. As the molar ratio of methylal to trioxane increased, the conversion of trioxane, which exceeds 90%, is basically unchanged. When the molar ratio of methylal to trioxane is less than 3, the selectivity of PODME<sub>3–8</sub> has a slight increase. However, when the molar ratio of methylal to trioxane increases from 3 to 6, the selectivity of PODME<sub>3–8</sub> sharply decreases from 69.61% to 48.15% (see Figure 3a).

As could be seen from Figure 3b, with increasing the molar ratio of methylal to trioxane, the selectivity of PODME<sub>2</sub> and PODME<sub>3</sub> rapidly increase, the selectivity of the PODME<sub>4</sub> and PODME<sub>5</sub> increase at first and then decrease, and the selectivity of PODME<sub>*n>6*</sub> gradually decreases. The selectivity of PODME<sub>*n*</sub> is in the sequence of  $n = 2 > n = 3 > n = 4 > n = 5 > n = 6 > n = 7 > n = 8$ , which also indicates the rationality of the reaction mechanism (Figure 2). As the amount of methylal increased,

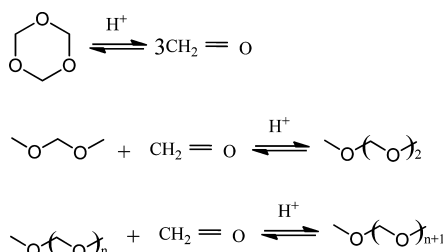
**Table 1. Brønsted Acid Strengths of Various Ionic Liquids<sup>a</sup>**

ionic liquid	$A_{\text{max}}$ (AU)	$[I]$ (%)	$[IH^+]$ (%)	$H_0$
<i>p</i> -nitroaniline	2.0523	100	0	
$[\text{PY-BS}][\text{HSO}_4^-]$	1.7301	84.3005	15.6995	1.7199
$[\text{PY-PS}][\text{HSO}_4^-]$	1.7320	84.3931	15.6069	1.7230
$[\text{MIM-BS}][\text{HSO}_4^-]$	1.7417	84.8658	15.1342	1.7388
$[\text{MIM-PS}][\text{HSO}_4^-]$	1.7513	85.3335	14.6665	1.7548
$[\text{TEA-BS}][\text{HSO}_4^-]$	1.7555	85.5382	14.4618	1.7619
$[\text{TEA-PS}][\text{HSO}_4^-]$	1.7700	86.2447	13.7553	1.7873

<sup>a</sup>Concentration, 20 mmol/L; indicator, *p*-nitroaniline;  $A_{\text{max}}$ , maximum absorbance of the indicator in various ionic liquid solutions;  $[I]$ , percentage of unprotonated *p*-nitroaniline;  $[IH^+]$ , percentage of protonated *p*-nitroaniline;  $H_0$ , Hammett function.



**Figure 1.** Effect of ionic liquids with different cations on the catalytic reaction. Reaction conditions:  $n(\text{methylal}):n(\text{trioxane}):n(\text{ILs}) = 180:60:1$ ;  $150^\circ\text{C}$ ; 10 h.



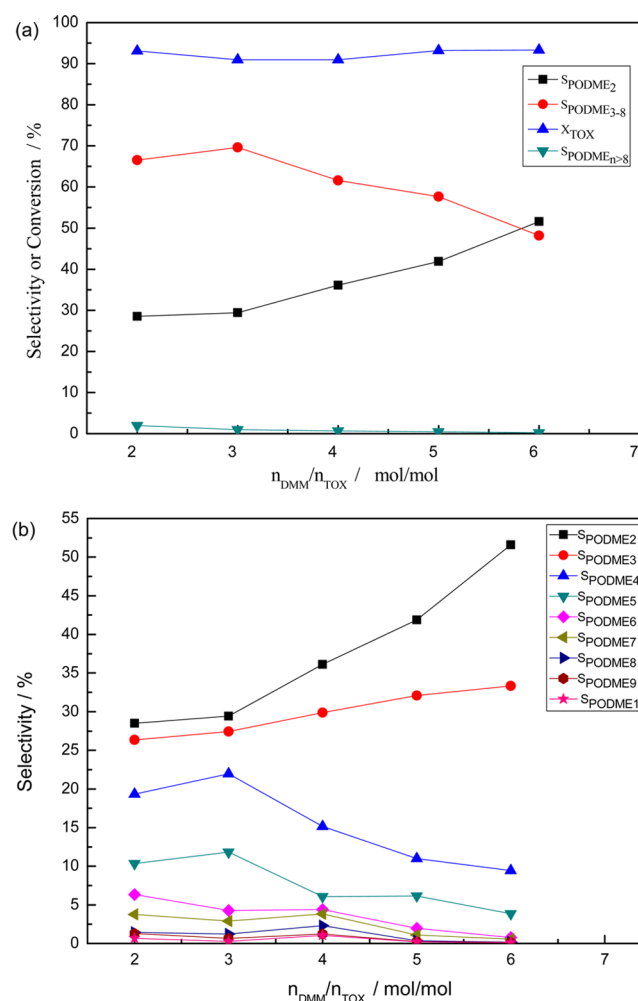
**Figure 2.** Reaction mechanism of PODME<sub>n</sub>.

formaldehyde, to which the trioxane is depolymerized, reacts easily with methylal, resulting in a higher rate of low degree of polymerization reaction. Therefore, the selectivity of PODME<sub>2-3</sub> is rapidly increased. In addition, on the basis of the reaction mechanism, formaldehyde is inserted into reaction

products of lower polymerization degree to form the products of higher polymerization degree. Therefore, the reaction is a consecutive reaction. With the increase of methylal, the selectivity of higher polymerization degree products increases at first and then decreases. Thus, considering the reaction rate and the selectivity of PODME<sub>3-8</sub>, the optimum molar ratio of methylal to trioxane is 3, at which the conversion of trioxane is 90.95%, and the product contains 69.61% of PODME<sub>3-8</sub> and only a trace amount of PODME<sub>n>8</sub>.

**3.2.3. Effect of Amount of Ionic Liquid.** A series of experiments were conducted using the best catalyst [PY-BS][HSO<sub>4</sub><sup>-</sup>] with different dosages (Figure 4). The amount of [PY-BS][HSO<sub>4</sub><sup>-</sup>] is denoted by the IL/methylal molar ratio. As shown in Figure 4a, when the IL/methylal molar ratio is less than 0.011, with an increase in the relative amount of ionic liquids, the rate of reaction is enhanced, resulting in a higher

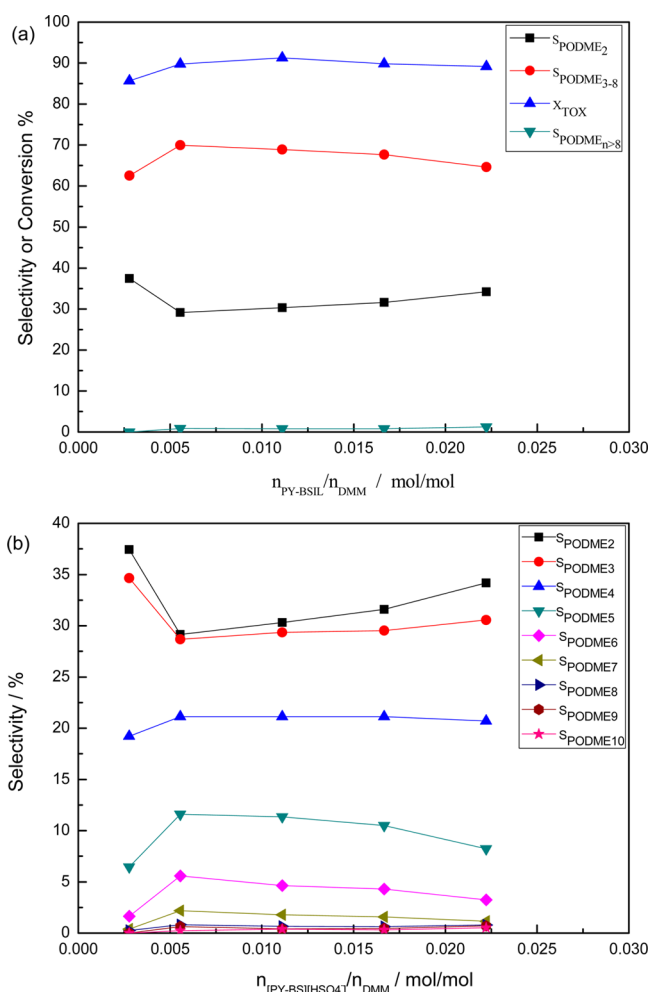




**Figure 3.** Effect of methylal/trioxane molar ratio on the catalytic reaction. Reaction conditions:  $n(\text{ILs}):n(\text{methylal}) = 1:180$ ;  $150^\circ\text{C}$ ; 10 h.

conversion of trioxane. This is attributed to the increase in acidity in the reaction system. However, when the IL/methylal molar ratio is more than 0.011, the conversion of trioxane is basically unchanged, which indicates that the depolymerization reaction has probably approached equilibrium. As shown in Figure 4a,b, when the molar ratio of IL to methylal increases, the selectivity of the  $\text{PODME}_{3-8}$  and  $\text{PODME}_{n\geq 4}$  increases at first and then decreases. When the molar ratio of IL to methylal is 0.00556, the selectivity of  $\text{PODME}_{3-8}$  and  $\text{PODME}_{n\geq 4}$  are up to maximum value. On the contrary, the selectivity of  $\text{PODME}_2$  and  $\text{PODME}_3$  are at a minimum value, which is attributed to the complex consecutive reaction catalyzed by acid ionic liquid. As a result, the optimal molar ratio of ILs to methylal (0.00556) is preferable.

**3.2.4. Effect of Reaction Time.** The effect of reaction time on the synthesis of  $\text{PODME}_n$  was investigated (see Figure 5). It can be seen that the conversion of trioxane and the selectivity of  $\text{PODME}_{3-8}$  and  $\text{PODME}_{n>8}$  increases significantly when the reaction time is extended. However, the selectivity of  $\text{PODME}_2$  decreases sharply. When reaction time is less than 6 h, with an increase in the reaction time, the conversion of trioxane and the selectivity of  $\text{PODME}_{3-8}$  shows a larger increase. However, when the reaction time is more than 8 h, they have a slight

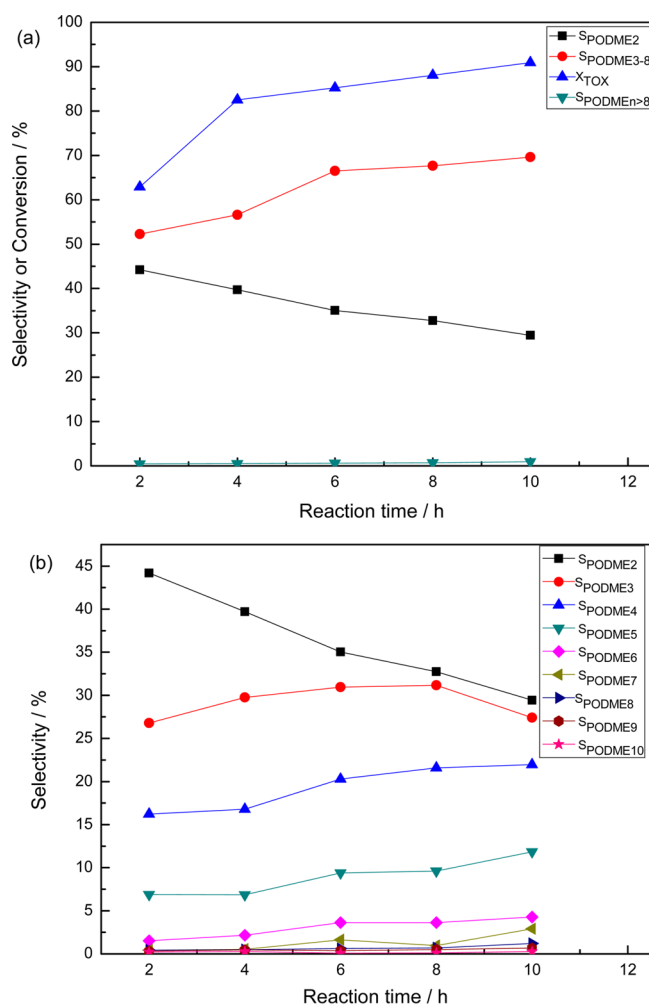


**Figure 4.** Effect of the amount of ionic liquid on the catalytic reaction. Reaction conditions:  $n(\text{methylal}):n(\text{trioxane}) = 3:1$ ;  $150^\circ\text{C}$ ; 10 h.

increase, which indicates that the rate of reaction is reduced and the reaction has probably approached equilibrium.

As shown in Figure 5b, with an increase in the reaction time, the selectivity of  $\text{PODME}_2$  gradually decreases and the selectivity of  $\text{PODME}_{n\geq 4}$  gradually increases. But the selectivity of  $\text{PODME}_3$  increases at first and then decreases, which is up to the maximum value when the reaction time is 8 h. This result is attributed to the reaction mechanism, which is a complex consecutive reaction. With an increase in reaction time, the conversion of trioxane has a slight increase and the depolymerization of trioxane becomes stable. On the basis of the reaction mechanism, formaldehyde is inserted into reaction products of lower polymerization degree to form the products of higher polymerization degree. The reaction is mainly polymerization degree growth. Therefore, with an increase in reaction time, a maximum peak appeared for the selectivity of lower polymerization degree, which is suitable for a complex consecutive reaction. For this reason, the optimum reaction time is 10 h.

**3.2.5. Effect of Reaction Temperature.** In general, the reaction temperature has an important effect on the kinetics and thermodynamics of the reaction. Therefore, the effect of reaction temperature on the synthesis of  $\text{PODME}_n$  was investigated (see Figure 6). With an increase of reaction temperature, the conversion of trioxane increases. However, although the temperature interval of the increase is equal, the

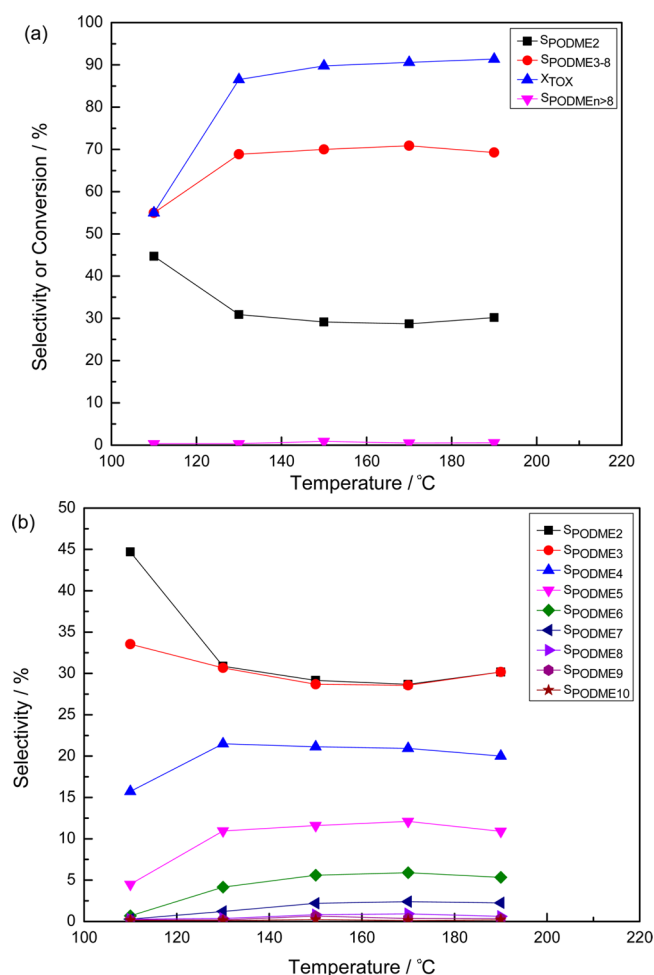


**Figure 5.** Effect of the reaction time on the synthesis of PODME<sub>n</sub>. Reaction conditions:  $n(\text{methylal}):n(\text{trioxane}):n(\text{ILs}) = 180:60:1$ ; 150 °C.

corresponding increased conversion reduces gradually. The selectivity of PODME<sub>2</sub> decreases at first and then increases, which is at a minimum value when reaction temperature is 170 °C. On the contrary, the selectivity of PODME<sub>3-8</sub> increases at first and then decreases, which is at a maximum value when reaction temperature is 170 °C. Similarly, the selectivity of PODME<sub>n>8</sub> increases at first and then decreases, which is at a maximum value when reaction temperature is 150 °C.

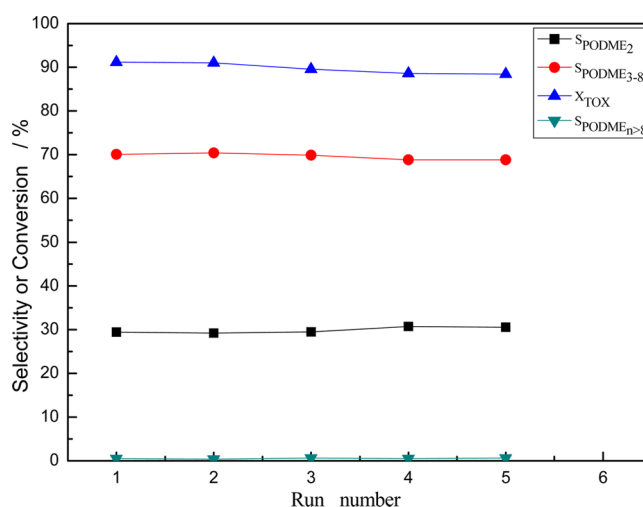
As can be seen from Figure 6b, the selectivity of PODME<sub>2</sub> and PODME<sub>3</sub> reduce at first and then increase, which is at a minimum when reaction temperature is 170 °C. On the contrary, the selectivity of PODME<sub>4</sub> increases at first and then decreases, which is at a maximum when reaction temperature is 130 °C. Similarly, the selectivity of PODME<sub>n≥5</sub> is at a maximum when reaction temperature is 170 °C. The depolymerization of trioxane is an endothermic reaction, and higher temperature is beneficial to the synthesis of formaldehyde. However, the reaction of chain length increase is an exothermic reaction and the increase of temperature will reduce the reaction performance. For this reason, the preferred reaction temperature is 170 °C.

**3.2.6. Reuse of Ionic Liquid.** In order to investigate the potential reusability of the ionic liquids in the synthesis of PODME<sub>n</sub>, a series of recycle experiments were conducted with



**Figure 6.** Effect of reaction temperature on the synthesis of PODME<sub>n</sub>. Reaction conditions:  $n(\text{methylal}):n(\text{trioxane}):n(\text{ILs}) = 180:60:1$ ; 10 h.

a methylal-to-trioxane molar ratio of 3 and ionic liquid-to-methylal molar ratio of 0.00556 at 170 °C for 10 h. After each recycle reaction, the ionic liquid was simply separated from the upper phase by decantation and was dried for 12 h in vacuum. As shown in Figure 7, the [PY-BS][HSO<sub>4</sub><sup>-</sup>] was used five times and its catalytic activity changed very little. Therefore, the [PY-



**Figure 7.** Reuse of ionic liquid.

BS][HSO<sub>4</sub><sup>-</sup>] as the catalyst for the synthesis of PODME<sub>n</sub> is recyclable and stable.

#### 4. CONCLUSIONS

Several ionic liquids with alkanesulfonic acid groups were synthesized successfully and were characterized by IR, NMR, ESI-MS, TG-DTA, and UV-vis spectroscopy. Catalytic reaction of methylal with trioxane for preparation of PODME<sub>n</sub> were investigated in various ionic liquids with alkanesulfonic acid groups. It was found that their structures were consistent with the designed structures. These acidic ionic liquids showed excellent catalytic performance for synthesis of PODME<sub>n</sub>. The catalytic activity of ILs is dependent on the different nitrogen groups of cations and the alkyl group length of ionic liquids. Increased Brønsted acidity gave improved catalytic activity. [PY-BS][HSO<sub>4</sub><sup>-</sup>] showed the best catalytic activity. From various parametric studies, such as dosage of the ionic liquid, molar ratio of DMM to TOX, and reaction temperature, optimum reaction conditions were established. The Brønsted acidic ionic liquids have a potential application in the production of PODME<sub>n</sub>.

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##### Notes

The authors declare no competing financial interest.

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