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Brønsted-acidic ionic liquids as efficient catalysts for the synthesis of polyoxymethylene dialkyl ethers



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ABSTRACT

Acetalation of formaldehyde (HCHO) with dialkyl formal or aliphatic alcohol to prepare polyoxymethylene dialkyl ethers (RO(CH₂O)_nR, $n \ge 1$) catalyzed by Brønsted-acidic ionic liquids has been developed. The correlation between the structure and acidity activity of various ionic liquids was studied. Among the ionic liquids investigated, 1-(4-sulfonic acid)butyl-3-methylimidazolium hydrogen sulfate ([MIMBs]HSO₄) exhibited the best catalytic performance in the reaction of diethoxymethane (DEM₁) with trioxane. The influences of ionic liquid loading, molar ratio of DEM₁ to HCHO, reaction temperature, pressure, time, and reactant source on the catalytic reaction were explored using [MIMBs]HSO₄ as the catalyst. Under the optimal conditions of $n([MIMBs]HSO_4):n(DEM_1):n(HCHO) = 1:80:80, 140 \,^{\circ}C$, and 4 h, the conversion of HCHO and selectivity for DEM₂₋₈ were 92.6% and 95.1%, respectively. The [MIMBs]HSO₄ catalyst could be easily separated and reused. A feasible mechanism for the catalytic performance of [MIMBs]HSO₄ was proposed.

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1. Introduction

Polyoxymethylene dialkyl ethers (RO(CH₂O)_nR, $n \ge 1$) are polyether compounds with high oxygen contents and cetane numbers (CN), and are regarded as a promising diesel additive to improve the combustibility of diesel oil, enhance combustion efficiency, and lower the release of pollutants [1,2]. It has been reported that the emission of particulate matter and NO_x released upon combustion were lowered by 80%–90% and 50%, respectively, when polyoxymethylene dimethyl ethers (CH₃O(CH₂O)_nCH₃, n = 3–8, PODE_{3–8}, DMM_{3–8}) were added to diesel oil with a ratio of 20% [2]. The CN, calorific value, and flashing point gradually increase and density and condensation point decrease with increasing R chain length of RO(CH₂O)_nR [3]. RO(CH_2O)_nR also can display excellent solubilizing power, permeating ability, and miscibility with most organic compounds. Furthermore, they are very promising for use as green industrial solvents and pigment dispersants.

RO(CH₂O)_{*n*}R can be synthesized from the end–group (–R) provider (e.g., aliphatic alcohol or dialkyl formal) and a compound that offers an oxymethylene group (–CH₂O–) as a chain segment, e.g., 1,3,5-trioxane (TOX), paraformaldehyde (PF), or formaldehyde (FA) [4]. In 1948, Gresham et al. [5] reported the first acetalation reaction of dialkyl formal with PF using a proton acid such as sulfuric acid as the catalyst, which mainly produced RO(CH₂O)_{*n*}R with n = 2 or 3. Subsequently, there have been many reports on the synthesis of PODE_{*n*}. For example, Renata et al. [6–9] patented the acetalation reaction of PF or

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TOX with methanol or methylal catalyzed by sulfuric or triflic acid. Heavy corrosion, difficult separation and recovery, and disposal of the spent catalyst are the disadvantages associated with the reported methods involving proton acid catalyst systems. To solve these problems, more environmentally friendly and easily separable solid acids, such as ion exchange resin Amberlyst 36 [10], cation resin NKC-9 [11], and molecular sieves [12–14] have been used as catalysts in PODE_n formation. Unfortunately, the reported catalytic systems still suffer from one or more disadvantages, including poor reactivity (low catalytic activity and selectivity) and easy deactivation.

Recently, ionic liquids (ILs) have attracted great interest as a novel catalyst because of their favorable properties. ILs combine the advantageous characteristics of both homogenous and heterogeneous catalysts, such as high acidic or alkali density, wide liquid range, uniform catalytic active sites, easy separation, and reusability [15]. As a result, ILs have been widely used in catalytic processes such as material synthesis, organic reactions, and biomass conversion [16-22]. Our group developed a method to synthesize PODE₃₋₈ using acidic ILs as catalysts with TOX, PF, or FA and methanol or methylal as raw materials [23-28]. Recently, acid ILs [PyBs]HSO₄ and [MIMBs]HSO₄ have been reported as catalysts for acetalation of TOX and methylal [29]. The conversion of TOX and selectivity of PODE₃₋₈ were 91.2% and 70.9%, respectively, under the conditions of n(ILs):n(methylal):n(TOX) = 1:180:60, 170 °C, and 10 h. Here, we investigate the potential applications of Brønsted-acidic IL in the acetalation reaction of FA and diethoxymethane $(C_2H_5OCH_2OC_2H_5, DEM_1)$ or aliphatic alcohol $(C_nH_{2n+1}OH, n \ge 2)$ (Scheme 1). Ideal yields of $RO(CH_2O)_n R$ (n = 2-8) are obtained in the presence of -SO₃H functionalized ILs and a possible reaction mechanism for this reaction system is proposed based on the experimental results. The recyclability of the catalyst system is also examined.

2. Experimental

2.1. General

All chemicals were analytical grade and used without further purification. Both ¹H and ¹³C NMR spectra were recorded on a Bruker AVIII HD 400 MHz NMR spectrometer (Switzerland) using tetramethylsilane as an internal standard. Fourier transform infrared (FT-IR) measurements were performed using KBr tablets on a Nicolet NEXUS 870 FT-IR infrared spectrometer (Madison, America). Absorbance spectra of 4-nitroaniline were obtained with a PerkinElmer Lambda 35 UV/VIS spectrometer (America).

2.2. Ionic liquid preparation

ILs were prepared according to a previous report [30] and their structures are shown in Scheme 1. A stoichiometric amount of 1,4-butane sultone, 1,3-propane sultone, bromobutane, or a solution of chloroacetic acid in chloroform was added dropwise to a stirred solution of *N*-methylimidazole, pyridine, or triphenylphosphine in toluene at room temperature, and



Scheme 1. Acetalation reaction of FA with dialkyl formal or aliphatic alcohol catalyzed by Brønsted-acidic ionic liquids.

then the mixture was heated at 60 °C for 12 h. The formed solid zwitterion was centrifuged and washed three times with toluene to remove unreacted non-ionic residues. After drying under vacuum (70 °C, 5.3 kPa, 12 h), white solid zwitterionic samples were obtained. A stoichiometric amount of concentrated sulfuric acid or methanesulfonic acid was then added dropwise to each zwitterionic sample in anhydrous toluene, and stirred at 80 °C for 12 h to form the IL. The IL phase was then washed repeatedly with toluene and dried under vacuum (70 °C, 5.3 kPa, 12 h) to give each viscous clear IL. When using *p*-toluenesulfonic acid (*p*-TSA) as the anion source, the preparation of ILs was carried out in water and the system was heated under reflux for 12 h. The mixture was dried under vacuum to form corresponding ILs.

NMR spectral data in CD₃OD or D₂O and FT-IR spectral data for ILs are presented as follows. Chemical shifts are reported in parts per million (ppm, δ) and referenced to D₂O (δ = 4.73) or CD₃OD (δ = 3.31).

[MIMBs]HSO4. ¹H NMR (400 MHz, D₂O): δ 1.66 (h, *J* = 8.0 Hz, 2H), 1.94 (h, *J* = 7.0 Hz, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 4.16 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 4.0 Hz, 1H), 8.64 (s, 1H). ¹³C NMR (100 MHz, D₂O): δ 21.0, 28.14, 35.75, 49.0, 50.14, 122.25, 123.75, 136.09. IR (KBr, ν /cm⁻¹): 3156 (C–H stretching vibration, MIM), 2963 (C–H stretching vibration, CH₂), 1572 (C=N stretching vibration, MIM), 1461 (C–H bending vibration, CH₃–N), 1229 (SO₂ stretching vibration, –SO₃H), 1168, 1054 (S=O stretching vibration, –SO₃H), 746 (C–C rocking vibration, (CH₂)_n, $n \ge 4$), 584 (–SO₃H, absorption peak).

[MIMBs]*p*-TSA. ¹H NMR (400 MHz, D₂O): δ 1.56 (h, *J* = 7.7 Hz, 2H), 1.84 (h, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 2.77 (t, *J* = 7.6 Hz, 2H), 3.70 (s, 3H), 4.05 (t, *J* = 7.0 Hz, 2H), 7.19 (d, *J* = 6.4 Hz, 2H), 7.24 (d, *J* = 3.6 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 8.54 (s, 1H). ¹³C NMR (100 MHz, D₂O): δ 20.39, 20.82, 27.99, 35.53, 48.79, 49.95, 122.03, 123.53, 125.23, 129.34, 135.79, 139.34, 142.35. IR (KBr, *v*/cm⁻¹): 3154 (C–H, MIM), 2958 (C–H, CH₂), 1570 (C=N, MIM), 1459 (C–H, CH₃–N), 1229 (SO₂, –SO₃H), 1168, 1033 (S=O, –SO₃H), 760 (C–C, (CH₂)*n*, *n* ≥ 4), 616 (–SO₃H).

[MIMBs]CH₃SO₃. ¹H NMR (400 MHz, D₂O): δ 1.60 (h, *J* = 8.0 Hz, 2H), 1.88 (h, *J* = 7.0 Hz, 2H), 2.66 (s, 3H), 2.80 (t, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 4.11 (t, *J* = 6.0 Hz, 2H), 7.30 (s, 1H), 7.36 (s, 1H), 8.60 (s, 1H). ¹³C NMR (100 MHz, D₂O): δ 20.96, 28.11, 35.70, 38.50, 48.95, 50.10, 122.21, 123.70, 135.97. IR (KBr, ν /cm⁻¹): 3154 (C-H, MIM), 2958 (C-H, CH₂), 1573 (C=N, MIM), 1461 (C-H, CH₃-N), 1194 (SO₂, -SO₃H), 1172, 1052 (S=O, -SO₃H), 651 (C-C, (CH₂)_n, $n \ge 4$), 557 (-SO₃H).

[MIMPs]HSO4. ¹H NMR (400 MHz, D₂O): δ 2.17 (h, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 4.22 (t, *J* = 6.0 Hz, 2H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.38 (d, *J* = 3.6 Hz, 1H), 8.60 (s, 1H). ¹³C NMR (100 MHz, D₂O): δ 25.08, 35.74, 47.26, 47.77, 122.20, 123.81, 136.15. IR (KBr, ν/cm^{-1}): 3158 (C–H, MIM), 2965 (C–H, CH₂), 1572 (C=N, MIM), 1461 (C–H, CH₃–N), 1131 (SO₂, –SO₃H), 1170, 1028 (S=O, –SO₃H), 749 (C–C rocking vibration, (CH₂)_n, *n* = 3), 579 (–SO₃H).

[PyBs]HSO₄. ¹H NMR (400 MHz, D₂O): δ 1.68 (h, *J* = 8.0 Hz, 2H), 2.06 (h, *J* = 7.0 Hz, 2H), 2.84 (t, *J* = 8.0 Hz, 2H), 4.54 (t, *J* = 8.0 Hz, 2H), 7.96 (t, *J* = 6.0 Hz, 2H), 8.43 (t, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, D₂O): δ 20.90, 29.31, 50.0, 61.23, 128.36, 144.25, 145.74. IR (KBr, ν/cm^{-1}): 3070 (C–H stretching vibration, Py), 2948 (C–H, CH₂), 1636 (C=N stretching vibration, Py), 1490 (C=C stretching vibration, Py), 1232 (SO₂, –SO₃H), 1171, 1033 (S=O, –SO₃H), 729 (C–C, (CH₂)_n, $n \ge 4$), 577 (–SO₃H).

[TENBs]HSO4. ¹H NMR (400 MHz, D₂O): δ 1.12 (t, *J* = 8.0 Hz, 9H), 1.68 (h, *J* = 8.0 Hz, 4H), 2.82 (t, *J* = 6.0 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H), 3.13 (q, *J* = 4.0 Hz, 6H). ¹³C NMR (100 MHz, D₂O): δ 6.66, 19.97, 21.25, 50.06, 52.66, 56.03. IR (KBr, *v*/cm⁻¹): 2994 (C-H stretching vibration, R), 1488, 1397 (C-H bending vibration, R), 1232 (SO₂, -SO₃H), 1163, 1034 (S=O, -SO₃H), 730 (C-C, (CH₂)_n, *n* ≥ 4), 578 (-SO₃H).

[TTPBs]HSO₄. ¹H NMR (400 MHz, CD₃OD): δ 1.87 (h, *J* = 8.0 Hz, 2H), 1.98 (h, *J* = 7.0 Hz, 2H), 2.86 (t, *J* = 6.0 Hz, 2H), 3.44 (t, *J* = 8.0 Hz, 2H), 7.72–7.77 (m, *J* = 4.0 Hz, 9H), 7.80 (t, *J* = 6.0 Hz, 3H), 7.86 (t, *J* = 6.0 Hz, 3H), ¹³C NMR (100 MHz, CD₃OD): δ 19.89, 25.43, 47.18, 47.39, 47.60, 47.82, 48.03, 130.0, 133.50, 134.87. IR (KBr, ν /cm⁻¹): 3061 (C–H stretching vibration, Ph), 2927 (C–H, R), 1568, 1484, 1438 (benzene skeleton vibration), 1241 (SO₂, –SO₃H), 1114, 1019 (S=O, –SO₃H), 725 (C–C, (CH₂)_n, $n \ge 4$), 605 (–SO₃H).

[MIMAc]HSO₄. ¹H NMR (400 MHz, D₂O): δ 3.83 (s, 3H), 5.03

(s, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 8.69 (s, 1H). ¹³C NMR (100 MHz, D₂O): δ 35.94, 49.85, 123.52, 137.40, 169.93. IR (KBr, v/cm⁻¹): 3119 (C–H, MIM), 2965 (C–H, CH₂), 2543–2620 (O–H stretching vibration, –COOH), 1742 (C=O, stretching vibration, –COOH), 1579 (C=N, MIM), 1413 (C–H, CH₃–N), 1173 (CO₂, stretching vibration, –COOH).

[MIMB]HSO4. ¹H NMR (400 MHz, D₂O): δ 0.79 (t, *J* = 8.0 Hz, 3H), 1.18 (m, *J* = 4.8 Hz, 2H), 1.72 (h, *J* = 8.0 Hz, 2H), 3.76 (s, 3H), 4.07 (t, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.55 (s, 1H), 8.57 (s, 1H). ¹³C NMR (100 MHz, D₂O): δ 12.64, 18.75, 31.26, 35.67, 49.30, 122.25, 123.52, 135.83. IR (KBr, ν/cm^{-1}): 3152 (C–H, MIM), 2963 (C–H, CH₂), 1571 (C=N, MIM), 1464 (C–H, CH₃–N), 753 (C–C, (CH₂)*n*, *n* ≥ 4).

2.3. Typical acetalation procedure

In a typical experiment, DEM₁ (0.6 mol), TOX (0.2 mol), and IL (7.5 mmol) were mixed together in a 120-mL Teflon-lined stainless-steel autoclave equipped with a thermometer and mechanical stirrer, then the autoclave was sealed up and flushed three times with N_2 . N_2 was introduced with initial pressure of 1.0-1.2 MPa at room temperature and the reaction was performed at 140 °C/2.0 MPa for the specified time. After the reaction, the autoclave was cooled to room temperature and the IL was separated from the reaction mixture through layering. The final products were identified and quantitatively analyzed by gas chromatography/mass spectrometry (GC/MS) (Agilent 7890A/5975C) and GC (Agilent 6890 equipped with a SE-54 capillary column), respectively. A known amount of furanidine was added as an internal standard to the product mixture before GC analysis. To recycle the catalyst, two methods were used to separate the IL from the reaction system. The first was decantation, which recovered the IL so that it could be reused directly in subsequent reactions. The second involved extraction of the products with benzene and then recovery of the IL by rotary evaporation to remove the extractant before reuse in the next run.

3. Results and discussion

3.1. Acidity analysis of -SO₃H functionalized ILs

To investigate the relationship between the acidity of ILs and anions, the acid strengths of $-SO_3H$ functionalized ILs were determined by UV/VIS spectroscopy using 4-nitroaniline as a basic indicator according to a previous report [31]. The Hammett function (H_0), which could be regarded as the relative acidity of the IL, was calculated using the equation $H_0 = pK(A)_{aq} + lg([A]_s/[AH^+]_s)$.

Using the same concentrations of 4-nitroaniline (2.5 mg/L, $pK_a = 0.99$) and IL (10 mmol/L) in ethanol, the H_0 values of the ILs were determined. The absorption maximum of the unprotonated form of 4-nitroaniline was observed at 372.8 nm in ethanol. When an IL was added, the absorbance of the unprotonated form of 4-nitroaniline decreased. As shown in Fig. 1, the absorbance of the unprotonated form of 4-nitroaniline in the presence of the three ILs decreased as follows:



Fig. 1. Absorbance spectra of 4-nitroaniline (A) for various $-SO_3H$ functionalized ILs in ethanol.

[MIMBs]HSO₄ > [MIMBs]*p*-TSA > [MIMBs]CH₃SO₃. After the calculation, we obtained the acidity order of the three ILs with the following H_0 values (Table 1): [MIMBs]HSO₄ (1.93) > [MIMBs]*p*-TSA (2.06) > [MIMBs]CH₃SO₃ (2.70), which is consistent with the acidity sequence of the anion precursors.

3.2. Effect of ionic liquid type on acetalation of DEM1 and TOX

First, a probe reaction of DEM1 and TOX was carried out at 140 °C and 2.0 MPa for 2 h catalyzed by these ILs (IL:HCHO = 1:80 molar ratio, a TOX molecule is considered as three HCHO ones) and the results are shown in Table 2. The main products were polyoxymethylene diethyl ethers $(C_2H_5O(CH_2O)_nC_2H_5)$ DEM_n , n = 2-8); byproducts of ethanol, ethyl formate, and ether were also detected in the reaction mixture. The catalytic activities of the ILs were affected by their structures. ILs bearing an alkyl sulfonic acid group on the cations exhibited higher activity than the one without this group even though it had the same anion (HSO4-) (Table 2, entries 1-5 vs. entries 6 and 7). Good conversion of FA (containing TOX and FA, > 83%) and selectivity for DEM₂₋₈ (> 94%) were obtained at 140 °C and 2.0 MPa for 2 h, and the selectivity for DEM_n decreased with increasing polymerization degree. The carbon chain length between the -SO₃H group and cation core had a slight effect on catalytic

Table 2

Effect of I	l.s with	different	structures	on the	reaction
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Table 1

Calculation and comparison of H_0 values of different $-SO_3H$ functionalized ILs in ethanol.

Ionic liquid	[A] (%)	[AH+] (%)	H_0	_
A ^a	100	0	_	
[MIMBs]HSO4	89.7	10.3	1.93	
[MIMBs]p-TSA	92.1	7.9	2.06	
[MIMBs]CH ₃ SO ₃	98.1	1.9	2.70	
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^a 4-Nitroaniline.

efficiency (Table 2, entry 1 vs. entry 2) and [MIMBs]HSO₄ functionalized with –SO₃H appeared to be the best catalyst with 87.4% conversion of FA and 95.0% selectivity for DEM₂₋₈ (Table 2, entry 1). The effect of ILs with different anions on the catalytic reaction was also studied. The catalytic performance of ILs functionalized with –SO₃H and with HSO₄⁻ as the anion appeared to be superior to that of the ILs with *p*-(CH₃)C₆H₄SO₃⁻ or CH₃SO₃⁻ as the anion in this reaction when they have the same cation (Table 2, entry 1 vs. entries 8 and 9). The catalysts displayed activities with the order of [MIMBs]HSO₄ > [MIMBs]*p*-TSA > [MIMBs]CH₃SO₃, which is consistent with the acidity sequence determined using H_0 (Table 1). These results suggest that the acidity of the ILs influenced its catalytic activity for acetalation reactions.

According to previous reports [11,12,32,33] and our results, a plausible mechanism for the formation of DEM_n is presented in Scheme 2. TOX is first converted to FA via hydrogen transfer along hydrogen bonds between the IL cation and TOX. The FA monomer reacts with DEM1 via a carbocation mechanism: DEM₁ is first protonated to generate the carbocation EtOCH₂₊. Adding FA molecules one by one to EtOCH2+ will cause the carbocation chain length to increase, and end-capping of the formed carbocations with ethanol will result in the generation of DEM_n with different chain lengths. Based on the analysis of the products, ethanol and FA were detected in the reaction mixture and the contents of DEM_n had the sequence of n = 2 > n= 3 > n = 4 > n = 5 > n = 6 > n = 7 > n = 8, which verifies that the reaction mechanism is reliable. The reaction rates for the acid-catalyzed decomposition of TOX correlated exactly with the Hammett acidity of the catalysts [34]. In addition, the insertion of FA into DEM_{n-1} to form DEM_n via a carbocation mechanism is

Entry	Catalwat	Product distribution (%)								Sele. for	Con. of					
	Catalyst -	DEM_1	DEM ₂	DEM ₃	DEM ₄	DEM ₅	DEM ₆	DEM ₇	DEM ₈	EtOH	DE ^a	EF ^b	TOX	FA	- DEM ₂₋₈ (%)	FА (%)
1	[MIMBs]HSO4	44.1	24.9	14.2	6.8	3.0	1.2	0.4	0.1	2.0	0.10	0.2	2.5	0.3	95.0	87.4
2	[MIMPs]HSO4	44.5	25.3	14.0	6.7	2.8	1.0	0.4	0.08	1.5	0.04	0.2	2.1	0.9	95.4	86.3
3	[PyBs]HSO4	46.3	24.8	13.0	6.0	2.4	0.9	0.3	0.1	1.9	0.04	0.2	2.9	0.7	94.2	83.7
4	[TPPBs]HSO4	44.0	24.6	13.6	6.8	3.2	1.4	0.5	0.2	2.0	0.04	0.1	2.9	0.5	95.0	84.9
5	[TENBs]HSO4	45.4	24.8	13.2	6.4	2.8	1.1	0.4	0.1	1.8	0.03	0.2	3.4	0.4	95.3	83.0
6	[MIMAc]HSO4	45.7	23.9	12.6	6.2	2.8	1.2	0.4	0.2	1.6	0.06	0.06	4.1	1.2	95.9	76.5
7	[MIMB]HSO ₄	63.2	15.1	3.5	0.7	0.1	0	0	0	1.7	0.03	0.3	14.0	1.3	89.0	31.8
8	[MIMBs]p-TSA	51.9	22.7	9.8	3.8	1.3	0.4	0.1	0.04	1.5	0.06	0.05	7.2	0.7	94.3	64.9
9	[MIMBs]CH ₃ SO ₃	60.0	17.0	4.7	1.3	0.4	0.2	0.05	0.03	0.4	0.06	0.2	14.6	0.4	95.4	33.1

Reaction conditions: ILs:HCHO(TOX):DEM1 = 1:80:80 molar ratio, 140 °C, 2.0 MPa, 2 h.

^a Ether. ^b Ethyl formate.



Scheme 2. The formation process of DEM_n from DEM₁ and TOX.

a typical acid-catalyzed reaction. Therefore, $-SO_3H$ functionalized ILs with strong acidity may be suitable catalysts for the target reaction.

3.3. Effect of reaction conditions on acetalation of DEM_1 and TOX

To optimize the reaction conditions of the acetalation of DEM_1 and TOX, the effects of catalyst loading, molar ratio of DEM_1 to HCHO (a TOX molecule is considered as three HCHO ones), reaction temperature, reaction pressure, and reaction time were also investigated using [MIMBs]HSO₄ as the catalyst; the results are summarized in Table 3.

The conversion of FA and the selectivity of DEM_{2-8} increased with catalyst mass (Table 3, entries 1–3), and the highest conversion of FA (87.4%) and selectivity for DEM_{2-8} (95.0%) were obtained when the molar ratio of [MIMBs]HSO₄ to HCHO was 1:80 (Table 3, entry 3). Upon further increasing the catalyst mass, the conversion of FA and selectivity for DEM_{2-8} decreased. This behavior indicates that it was important to use a suitable amount of catalyst in this acetalation

Table 3

Effect of reaction conditions using [MIMBs]HSO₄ as catalyst.



Fig. 2. Contents of DEM_n dependence of [MIMBs]HSO₄:HCHO molar ratio. Reaction conditions: HCHO(TOX):DEM₁ = 1:1 molar ratio, 140 °C, 2.0 MPa, 2 h.

reaction. Excess acid may promote depolymerization reactions, which produce a large number of byproducts such as ethanol and FA. In addition, as shown in Fig. 2, the contents of DEM_{1-8} in the reaction solution remained almost unchanged as the molar ratio of [MIMBs]HSO₄ to HCHO changed from 1:120 to 1:80, and the contents of DEM_{3-6} increased as the molar ratio of [MIMBs]HSO₄ to HCHO increased from 1:80 to 1:60. Therefore, the optimum molar ratio of [MIMBs]HSO₄ to HCHO is 1:80.

The molar ratio of DEM₁ to HCHO also played an important role in the efficiency of the acetalation reaction. The results showed that the conversion of FA increased with the molar ratio of DEM₁ to HCHO, and reached its maximum of 87.4%when the DEM₁:HCHO molar ratio was 1:1 (Table 3, entry 3).

P	IL:HCHO	DEM ₁ :HCHO	Temperature	Pressure	Time	Con. of FA	Sele. for DEM ₂₋₈
Entry	(molar ratio)	(molar ratio)	(°C)	(MPa)	(min)	(%)	(%)
1	1:120	1:1	140	2.0	120	76.7	94.8
2	1:100	1:1	140	2.0	120	82.0	95.8
3	1:80	1:1	140	2.0	120	87.4	95.0
4	1:60	1:1	140	2.0	120	85.6	93.7
5	1:80	0.8:1	140	2.0	120	85.9	94.6
6	1:80	1.2:1	140	2.0	120	84.6	94.8
7	1:80	1.4:1	140	2.0	120	81.3	95.8
8	1:80	1.6:1	140	2.0	120	76.8	94.9
9	1:80	1:1	100	2.0	120	35.4	91.2
10	1:80	1:1	120	2.0	120	68.7	94.2
11	1:80	1:1	130	2.0	120	82.5	95.1
12	1:80	1:1	150	2.0	120	84.0	90.6
13	1:80	1:1	140	Self-pressure	120	81.4	94.1
14	1:80	1:1	140	1.0	120	85.1	93.7
15	1:80	1:1	140	3.0	120	87.3	95.1
16	1:80	1:1	140	2.0	20	40.4	92.8
17	1:80	1:1	140	2.0	40	56.4	92.3
18	1:80	1:1	140	2.0	60	60.7	93.5
19	1:80	1:1	140	2.0	80	73.8	93.0
20	1:80	1:1	140	2.0	100	79.6	92.8
21	1:80	1:1	140	2.0	180	90.1	95.0
22	1:80	1:1	140	2.0	240	92.6	95.1

Reaction conditions: the source of formaldehyde is trioxane.



Fig. 3. Contents of DEM_n dependence of DEM_1 :HCHO molar ratio. Reaction conditions: ILs:HCHO(TOX) = 1:80 molar ratio, 140 °C, 2.0 MPa, 2 h.

Then, the conversion gradually decreased as the amount of DEM₁ continued to increase, which was probably caused by the dilution of the IL catalyst with the excess reactant. The selectivity for DEM₂₋₈ was unchanged regardless of the molar ratio of DEM₁ to HCHO. The optimum molar ratio of DEM₁:HCHO is 1:1, at which the conversion of FA is 87.4%, and the selectivity for DEM₂₋₈ is 95.0%. As illustrated in Fig. 3, with increasing molar ratio of DEM₁ to HCHO, the contents of DEM₃₋₆ in the reaction solution gradually decreased.

Reaction temperature had a dramatic effect on the reaction outcome. When the temperature was increased from 100 to 140 °C, the conversion of FA and selectivity for DEM₂₋₈ increased from 35.4% to 87.4% and 91.2% to 95.0%, respectively (Table 3, entries 3 and 9–11). As the temperature rose further, the conversion of FA and selectivity for DEM₂₋₈ decreased because of the depolymerization reactions of the products to form more byproducts at higher temperature. Fig. 4 reveals that the contents of DEM₂₋₈ first increased and then decreased, approaching the maximum value when the reaction temperature was 140 °C. The depolymerization of TOX is an endothermic reaction, so higher temperature is favorable for it. However, higher temperature will limit the chain length increase of DEM_n, which is an exothermic reaction. For this reason, the optimal reaction temperature is 140 °C.



Fig. 4. Contents of DEM_n at different temperature. Reaction conditions: ILs:HCHO(TOX):DEM₁ = 1:80:80 molar ratio, 2.0 MPa, 2 h.



Fig. 5. Contents of DEM_n under different pressures. Reaction conditions: ILs:HCHO(TOX):DEM₁ = 1:80:80 molar ratio, 140 °C, 2 h.

The influence of pressure on the reaction was not obvious. At self-pressure, the conversion of FA and selectivity for DEM₂₋₈ were 81.4% and 94.1%, respectively (Table 3, entry 13). With increasing reaction pressure, the reaction was slightly promoted, reaching good conversion of FA and selectivity for DEM₂₋₈ of 87.4% and 95.0% at 2.0 MPa, respectively (Table 3, entry 3). Further increasing the pressure to 3.0 MPa caused the conversion and selectivity to change very little (Table 3, entry 15). Fig. 5 reveals that pressure had little influence on the contents of DEM₂₋₈.

The effect of reaction time on the synthesis of DEM_n was also investigated in the range from 20 min to 4 h. Prolonging reaction time was propitious for the reaction (Table 3, entries 3 and 16–22). Increased conversion of FA and selectivity for DEM_{2-8} were observed when the reaction time was extended, and reached 87.4% and 95.0%, respectively, at 2 h (Table 3, entry 3). Further prolonging the reaction time resulted in only slight increases of the conversion of FA and selectivity for DEM_{2-8} . As shown in Fig. 6, with lengthening reaction time, the content of DEM_2 in the reaction solution first increased and then decreased, reaching the maximum value when the reaction time was 100 min. When the reaction time was less than 2 h, with extending reaction time, the contents of DEM_{3-6} gradu-



Fig. 6. Contents of DEM_n at different time. Reaction conditions: $ILs:HCHO(TOX):DEM_1 = 1:80:80$ molar ratio, 140 °C, 2.0 MPa.

ally increased. However, when the reaction time was more than 2 h, they increased only slightly, which indicates that the reaction rate lowered and the reaction probably approached equilibrium. DEM₇ and DEM₈ were also detected in the reaction mixture after 1 and 2 h, respectively, and their contents increased over time. These experimental phenomena are attributed to the consecutive reaction mechanism of acetalation of DEM₁ with TOX. As the reaction time lengthened, the conversion and content of FA increased slightly, which indicates that the decomposition of TOX to FA becomes stable. The FA monomer inserted one by one into DEM_{n-1} to form DEM_n as the reaction proceeded.

3.4. Sources of FA and end-group providers

Using [MIMBs]HSO₄ as a catalyst, the sources of FA (i.e., TOX and PF) and the end-group (-R) provider (such as DEM1, ethanol, propanol, and butanol) were examined; the results are presented in Table 4. We found that although similar selectivity for DEM₂₋₈ was obtained using different forms of FA, TOX was the best supplier of FA for the reaction with the highest conversion (87.7%). When ethanol was used as the -R provider, the main products showed a lower polymerization degree of DEM_n and the selectivity for DEM2-8 decreased markedly, and the conversion of FA decreased to 80.4%. Water is a byproduct of the acetalation of FA with aliphatic alcohols, which easily causes hydrolysis of products and inhibits the occurrence of consecutive reactions. We studied the scope of the IL-catalyzed acetalation towards various aliphatic alcohols with TOX. The conversion of FA was 65.6% and the selectivities for $C_{3}H_{7}O(CH_{2}O)_{n}C_{3}H_{7}$ with n = 1, 2, 3, 4, 5, 6, and 7 were 60.0%, 23.8%, 8.9%, 2.9%, 0.9%, 0.2%, and 0.05%, respectively, when propanol was used as the -R provider at 140 °C and 2.0 MPa for 2 h. As for butanol, the conversion of FA was 73.2% and the selectivities for $C_4H_9O(CH_2O)_nC_4H_9$ with n = 1, 2, 3, 4, 5, 6, and 7 were 57.7%, 24.3%, 9.6%, 3.5%, 1.2%, 0.4%, and 0.1%, respectively. Reactivity increased with decreasing chain length of the aliphatic alcohols, and aliphatic alcohols with an even number of carbons displayed higher reactivity compared with those with an odd number of carbons.

3.5. Reusability of [MIMBs]HSO4 as a catalyst

A series of recycling experiments were conducted to investigate the recoverability and recyclability of the ILs functionalized with $-SO_3H$ in the acetalation reaction of dialkyl formal

Table 5

Recycling of [MIMBs]HSO₄ in the acetalation reaction of DEM₁ with TOX using different separation methods (layering and extraction).

	La	ayering		Extraction				
Run	Con. of FA	Sele. for DEM ₂₋₈		Con. of FA	Sele. for DEM_{2-8}			
	(%)	(%)		(%)	(%)			
1	87.7	95.0		87.7	95.0			
2	82.6	94.5		83.5	95.7			
3	75.8	96.1		77.3	95.4			
4	67.3	95.1		68.5	94.8			
5	63.6	95.3		66.2	93.2			
6	57.4	95.5		64.4	94.5			
7	54.0	95.7		62.7	93.9			
8	47.8	95.2		61.8	94.5			

Reaction conditions: [MIMBs]HSO4:HCHO(TOX):DEM1 = 1:80:80 molar ratio, 140 °C, 2.0 MPa, 2 h.

with FA. In this paper, two methods, i.e., layering and extraction, were used to separate ILs from the reaction system. First, [MIMBs]HSO4 was separated from the reaction mixture through layering and reused in another cycle under the same conditions without any treatment. The reusability of the recycled catalyst is shown in Table 5. No obvious change was observed in the selectivity for DEM2-8, and the conversion of FA decreased from 87.7% to 47.8% after eight runs. Recovering the used catalyst by extraction of the products with *n*-hexane (5 mL×3) and vacuum drying for 12 h at 70 °C recovered 85.6% of [MIMBs]HSO4. Second, [MIMBs]HSO4 was separated by extraction of the products with benzene and then dried by rotary evaporation before reuse. After eight runs, the conversion of FA decreased from 87.7% to 61.8% and the recovery of [MIMBs]HSO₄ was 91.8%. In addition, the FT-IR spectrum of fresh [MIMBs]HSO4 is compared with that reused eight times in Fig. 7. The lack of obvious change of the three FT-IR spectra indicates that the structure of the [MIMBs]HSO4 catalyst hardly changed after reuse eight times. Therefore, the main reason for the observed decrease of catalytic activity is the loss of catalyst.

4. Conclusions

We demonstrated that Brønsted-acidic ILs can catalyze the acetalation reactions for the formation of polyoxymethylene dialkyl ethers under solvent–free conditions. ILs functionalized with –SO₃H showed the highest catalytic performance for the synthesis of polyoxymethylene dialkyl ethers. [MIMBs]HSO₄ showed the highest catalytic activity for acetalation of DEM₁ with TOX, giving the high conversion of FA (92.6%) and selec-

 Table 4

 Influence of different FA sources and the end-group (-R) providers on the reaction.

		0 10 11										
–R provider	-CH ₂ O- provider	Con. of FA (%)	Sele. for RO(CH ₂ O) _n R (%)									
			<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6	<i>n</i> = 7	<i>n</i> = 8		
DEM ₁	TOX	87.7	_	47.7	26.5	13.3	5.8	2.3	1.2	0.2		
DEM1	PF	86.6	_	48.4	26.1	12.9	6.0	2.5	1.0	0.4		
CH ₃ CH ₂ OH	TOX	80.4	56.9	23.0	8.3	2.6	0.7	0.2	0	0		
CH ₃ (CH ₂) ₂ OH	TOX	65.6	60.0	23.8	8.9	2.9	0.9	0.2	0.05	0		
CH3(CH2)3OH	TOX	73.2	57.7	24.3	9.6	3.5	1.2	0.4	0.1	0		

Reaction conditions: [MIMBs]HSO4:HCHO:R provider = 1:80:80 molar ratio, 140 °C, 2.0 MPa, 2 h.



Fig. 7. FT-IR spectra comparison of the fresh and the eight times reused [MIMBs]HSO₄. (1) Fresh [MIMBs]HSO₄; (2) [MIMBs]HSO₄ reused eight times (separation by layering); (3) [MIMBs]HSO₄ reused eight times (separation by extraction).

tivity for DEM_{2-8} (95.1%). The source of FA and -R provider were examined and a plausible reaction mechanism was proposed. The present study provides an environmentally friendly and high-yielding synthetic methodology to obtain polyoxymethylene dialkyl ethers.

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Graphical Abstract

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Brønsted-acidic ionic liquids as efficient catalysts for the synthesis of polyoxymethylene dialkyl ethers

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