Green Chemistry

Cite this: *Green Chem.*, 2011, **13**, 2786

www.rsc.org/greenchem

PAPER

Influence of Brønsted acid ionic liquid structure on hydroxyacid polyesterification

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Received 5th March 2011, Accepted 15th July 2011
DOI: 10.1039/c1gc15241f

Brønsted acid ionic liquids (BAILs) based on the 4-(3′-butyl-1′-imidazolio)-1-butanesulfonic acid cation were found to be very efficient polyesterification solvents and catalysts. Only 5–30 min at 90–110 °C was required to obtain high molar mass poly(12-hydroxydodecanoic acid) (M_w up to 40000 g mol^{-1}). The polyesterification was faster in BAILs with the bis(trifluoromethylsulfonyl)-imidide anion (Tf_2N), but small amounts of ethers and double bonds arising from side reactions were detected in the final polymer. On the other hand, no side reactions took place in the BAIL with the hydrogen sulfate anion, except for the formation of a sulfonate ester intermediate that can further react with carboxylic acid groups to yield the expected ester. This intermediate, not observed in Tf_2N-based BAILs, might be involved in the protection of hydroxy end groups from etherification side reactions in HSO_4^--based BAILs. To explain the different behaviors of these BAILs, and since the acidity of H_2SO_4 is much higher than that of Tf_2NH, it is suggested that the structure of these BAILs could be different: alkylsulfonic acid-substituted imidazolium for the former, while the latter could be just a mixture of imidazolium–sulfonate zwitterion and Tf_2NH. The influence of reaction temperature, water elimination method and BAIL concentration on polyesterification are also discussed.

Introduction

The conventional way to synthesize polyester is the bulk reaction between diols and diacids or diesters.[1,2] The process usually requires catalysts such as metal salts, metal oxides or metal alkoxides, and high temperature (170–300 °C) as well as long reaction time (several hours). Vacuum is often applied at the end of reaction to strip off the last traces of reaction water and to shift esterification equilibrium toward the formation of high molar mass polyesters. It must be underlined that metal-based catalysts cannot be removed and remain in final polymer. Alternatively, polyesters can be produced by solution reaction of diols and diacid chlorides or activated dicarboxylic acids in milder conditions and shorter reaction time.[2] In these processes, however, expensive and/or toxic starting monomers, activating agents and solvents are used. It is costly to remove solvents, as well as to dispose of activating agent residues.

Since the concept of green chemistry has emerged, much attention has been paid to organic chemistry processes involving ionic liquids (ILs) as non-volatile, easily recyclable reaction media of high thermal and chemical stabilities.[3–9] A number of polymerization processes, either chain polymerizations or polycondensations, have also been studied in ionic liquids.[10–12] Most polycondensation studies were relative to the synthesis of aromatic polymers such as polyamides, polyimides, polyhydrazides or polyoxadiazoles in a range of conventional ionic liquids.[13–21] Some syntheses of polyesters in ionic liquids have also been described: poly(glycolic acid) and copolymers of glycolic acid and ε-caprolactone were obtained by high temperature post-polycondensation of oligomers,[22,23] enzyme-catalyzed polyesterifications yielded low molar mass polyesters[24,25] and Wang *et al.*[26] used various dialkylimidazolium salts as catalysts in the bulk synthesis of poly(lactic acid). Fu and Liu[27] showed that high molar mass aliphatic polyesters could be obtained in di-akylimidazolium salts by post-polycondensation of oligoesters, but the two-step procedure required high temperature (160 °C), long reaction time (24 h) and the addition of a metal catalyst.

A specific category of ionic liquids, namely Brønsted acid ionic liquids (BAILs), were reported to play a double role of catalyst and solvent for various acid-catalyzed reactions and, especially, Fischer esterifications. Such reactions were carried out in BAILs with SO_3H-functionalized cations, such as phosphoniums,[28,29] ammoniums,[30–32] pyridiniums[30,33,34] or imidazoliums,[28,30] and/or acidic anions, such as hydrogen sulfate or dihydrogen phosphate.[30–37] High yield of ester, low reaction temperature and short reaction time are some of the advantages

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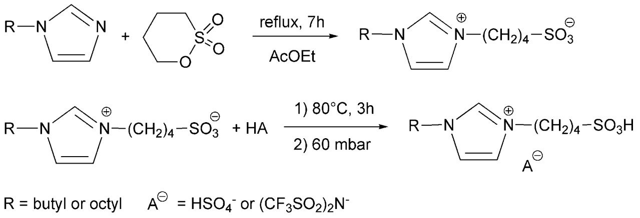
of the method. In a recent paper,[38] we reported the first synthesis of high molar mass polyesters in SO_3H-functionalized imidazoliums, at moderate temperature (90–110 °C) and for short reaction time.

The present paper investigates the effect of the imidazolium alkyl substituent, counterion, reaction time, temperature and BAIL concentration on the average molar masses of poly(12-hydroxydodecanoic acid), taken as an example. Polyester solubility and side reactions are also investigated. Besides, more importantly, we report here that different behaviors of the BAILs with different counterions were observed in the polyesterification of 12-hydroxydodecanoic acid. Potential reaction mechanisms are, therefore, also discussed.

Results and discussion

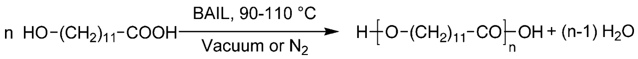
Three SO_3H-functionalized imidazolium-based BAILs with octyl or butyl substituents and hydrogen sulfate or bis(trifluoromethylsulfonyl)imidide counterions were used as both solvents and catalysts for the polyesterification of 12-hydroxydodecanoic acid (12-HDA). These BAILs, namely 4-(3′-butyl-1′-imidazolio)-1-butanesulfonic acid hydrogen sulfate ($[BBSIm]HSO_4$), 4-(3′-butyl-1′-imidazolio)-1-butanesulfonic acid bis(trifluoromethylsulfonyl)imidide ($[BBSIm]Tf_2N$) and 4-(3′-octyl-1′-imidazolio)-1-butanesulfonic acid bis(trifluoromethylsulfonyl)imidide ($[OBSIm]Tf_2N$), were synthesized in a straightforward two-step approach (Scheme 1):[28,30]

As generally observed when the length of the alkyl substituents of imidazolium-based ionic liquids increases,[39,40] the octyl-substituted imidazolium was more viscous than its butyl homologue. The viscosities of these BAILs were also significantly modified when the counterion was replaced: at room temperature, $[BBSIm]Tf_2N$ was much less viscous than $[BBSIm]HSO_4$.



Scheme 1 Two-step synthesis of SO_3H-functionalized BAILs.

The polyesterifications of 12-hydroxydodecanoic acid (12-HDA) were carried out at 90 or 100 °C using 12-HDA/BAIL equimolar amounts. Reaction water was eliminated either by flowing nitrogen over reaction medium or by applying vacuum (10 mbar) during the reaction (Scheme 2).



$$n\ HO{-}(CH_2)_{11}{-}COOH \xrightarrow[\text{Vacuum or } N_2]{\text{BAIL, 90-110 °C}} H{-}\!\left[O{-}(CH_2)_{11}{-}CO\right]_n\!{-}OH + (n\text{-}1)\ H_2O$$

Scheme 2 Polyesterification of 12-hydroxydodecanoic acid in BAIL.

A comparison between the reactions with and without BAIL is presented in Table 1, demonstrating that the polyesterification of 12-HDA in the BAILs is very efficient. When no catalyst was added (entry 1), polyesterification had to be carried out in harsh conditions, namely high temperature and long reaction time to obtain high-molar-mass polyesters. In the presence of *p*-toluenesulfonic acid catalyst, only low-molar-mass oligomers were obtained after 30 min reaction at 110 °C. On the other hand, when reaction was carried out in a BAIL (entries 3–6), high-molar-mass polyesters were obtained in 30 min at 90–110 °C. Moreover, it is worthwhile emphasizing that the reaction was so effective in $[BBSIm]Tf_2N$ that polyesters of M_w up to 40000 g mol^{-1} could be obtained after only 15 min. This clearly shows, therefore, the high efficiency of BAILs for 12-HDA polyesterification.

Solubility of poly(12-HDA) in BAILS

The dissolving ability of an ionic liquid depends largely on the structure of both its anion and its cation,[41] but little investigation has been carried out on the issue so far, especially on polymers. The polymerization of 12-HDA in each BAIL was followed under polarizing optical microscope (POM) at 110 °C. These experiments showed that the miscibility of poly(12-HDA) with the various BAILs was very different from each other. The 12-HDA monomer was soluble in $[BBSIm]HSO_4$ and in $[BBSIm]Tf_2N$ at 110 °C (Table 2). During polyesterification, the reaction medium became viscous and heterogeneous in the former, while it was always fluid, transparent and visually homogenous in the latter. However, two phases were detected when observing both reaction media under polarizing microscope (POM) during the reaction, as shown in Fig. 1a and 1c, where the bubble-like spots are molten poly(12-HDA) while the grey background is BAIL in each image. This could be interpreted as follows: as polymer chain increased, poly(12-HDA) became

Table 1 Polycondensation of 12-HDA: mass-average molar mass (M_w) calculated from SEC data, number-average molar mass (M_n) obtained from SEC data and ^1H NMR

Entry	BAIL or catalyst	T/°C	Time (min)	M_w (g mol^{-1})	$M_n{}^a$ (g mol^{-1})	$M_n{}^b$ (g mol^{-1})	Yield^g %
1	Nil^c	175	480	38700	15270	12060	95
2	*p*-TSA^{c,d}	110	30	5950	2290	2390	95
3	$[BBSIm]Tf_2N^f$	110	15	39010	18380	15180	96
4	$[BBSIm]HSO_4{}^e$	110	30	24910	10313	10140	86
5	$[BBSIm]Tf_2N^f$	90	30	39720	14420	12360	90
6	$[OBSIm]Tf_2N^e$	110	30	36110	14580	15680	92

^{a} Values from SEC in CH_2Cl_2 ^{b} Values from ^1H NMR ($CDCl_3$). ^{c} Reaction carried out in the bulk with 500 ml min^{-1} N_2 flow rate. ^{d} Reaction catalyzed by 1 wt-% *p*-TSA. ^{e} Reaction carried out in BAILs under vacuum (10 mbar). ^{f} Reaction carried out in BAILs under 500 ml min^{-1} N_2 flow. ^{g} Yield of isolated product.

Table 2 Homogeneity of 12-HDA/BAIL reaction media at 110 °C, as observed by polarizing optical microscope

	Homogeneity	
BAIL	12-HDA	poly(12-HDA)
[BBSIm]HSO_4	Homogeneous	Heterogeneous
[BBSIm]Tf_2N	Homogeneous	Heterogeneous
[OBSIm]Tf_2N	Homogeneous	Homogeneous

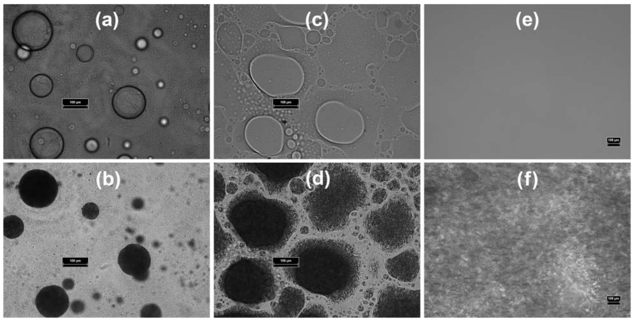


Fig. 1 Polarizing optical microscopy images of the reaction medium: [BBSIm]HSO_4 at (a) 110 °C and (b) room temperature, [BBSIm]Tf_2N at (c) 110 °C and (d) room temperature and [OBSIm]Tf_2N at (e) 110 °C and (f) room temperature (bar length = 100 μm).

more hydrophobic and less soluble in these hydrophilic ionic liquids. Upon cooling down to room temperature, poly(12-HDA) crystallized, resulting in a dispersion of solid polymer particles of 10 to 200 μm diameter in the ionic liquid (Fig. 1b and 1d).

The same test was carried out in the octyl-substituted ionic liquid [OBSIm]Tf_2N. It was observed under a polarizing microscope that both 12-HDA and poly(12-HDA) were soluble in this BAIL at 110 °C (Fig. 1e). Since poly(12-HDA) was not soluble in [BBSIm]Tf_2N, the length of the alkyl substituent of the imidazolium cation seems to play an important role on solubility. The presence of the octyl substituent increases the [OBSIm]Tf_2N hydrophobicity with respect to [BBSIm]Tf_2N, which could explain why poly(12-HDA) is more soluble in the former. Polymer precipitation during solution polycondensation generally hinders the formation of high MW polymers. However, this is usually observed for rigid, crystalline polymers. In the present case, poly-HDA precipitates in the molten state. Chains remain flexible and chain-ends reactive, which can explain why high MW poly-HDA was formed in this BAIL.

It should finally be noted that poly(12-HDA) was not soluble in any of the BAILs at room temperature (Fig. 1b, 1d, 1f), which facilitated polymer recovery.

Influence of temperature

Two series of experiments were carried out in [BBSIm]Tf_2N, respectively at 90 °C and 110 °C, and water was eliminated under vacuum (10 mbar) (Fig. 2). At the early stages, the polyesterification of 12-HDA was faster at 110 °C than at 90 °C. At 110 °C, polymer molar mass was already close to M_w = 35000 g mol^{-1} after only 5 min and reached a maximum of M_w close to 40000 g mol^{-1} after 15 min. As expected for a kinetically controlled polymerization, the reaction was slower at 90 °C and it took 30 min to reach its maximum of about 40000 g mol^{-1}.

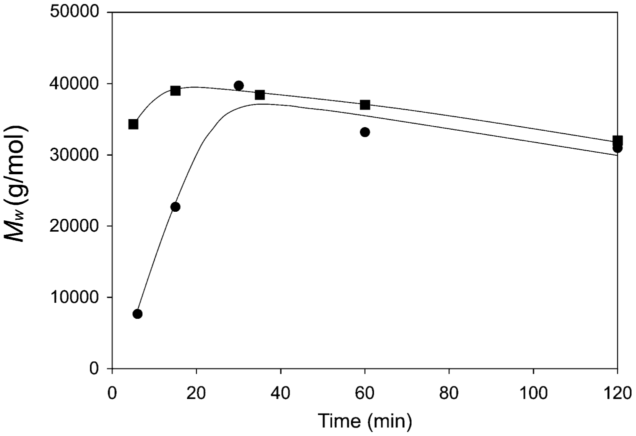


Fig. 2 Evolution of M_w at different temperatures in [BBSIm]Tf_2N: polyesterification of 12-HDA in [BBSIm]Tf_2N (12-HDA/BAIL molar ratio = 1/1) at 90 °C (●) or 110 °C (■) under vacuum (10 mbar).

Therefore, compared to traditional polyesterification in the bulk, which requires high temperature (≥ 170 °C) and long reaction time, the reaction in [BBSIm]Tf_2N boasts a significant advantage in terms of time and energy effectiveness. For conventional polyesterifications, a M_w plateau is reached at long reaction time, due to several factors: diffusion control of the reaction when polymer viscosity increases, reduced mass-transfer resulting in incomplete water elimination, stoichiometric unbalance due to side reactions or the presence of impurities. In the present case, almost the same results were found at both 110 °C and 90 °C, but instead of a plateau, a M_w decrease was observed. This point is discussed below.

Water elimination approaches

Due to the reversibility of polyesterification, water generated during the reaction is detrimental to molar mass growth. The water content of BAILs used in this study was about 0.5% by weight, only 1/10 of water formed during polyesterification of 12-HDA, which implies that it is reaction water that has more important influence on the molar mass. It is, therefore, very important to eliminate it. Moreover, according to Thomazeau *et al.*,[42] the presence of water could also decrease the acidity of the proton in BAILs, meaning that it could have a negative influence on their catalytic performance. In order to confirm the negative effect of water, a blank experiment was carried out without evaporating water in the reaction mixture. As shown in Table 3, when water remained in reaction medium (Entry 1), polymers of low molar mass were produced, whereas when water was stripped by either vacuum or N_2 flow, polyesterification was much more favored (Entries 2 and 3). The results obtained using vacuum (10 mbar) were close to those obtained with a nitrogen flow.

Comparison of polyesterifications in different BAILs

The polyesterification of 12-HDA carried out in [BBSIm]HSO_4 and in [BBSIm]Tf_2N at 110 °C under nitrogen flow gave very different results. As shown in Fig. 3, polyesterification was more efficient in [BBSIm]Tf_2N during the first 40 min, producing poly(12-HDA) of higher molar mass than that in [BBSIm]HSO_4.

Table 3 Polyesterification of 12-HDA in [BBSIm]Tf_2N (12-HDA/BAIL molar ratio = 1/1) at 110 °C for 2 h: mass-average molar mass (M_w) calculated from SEC data, number-average molar mass (M_n) obtained from SEC data and ^1H NMR

Entry	Water elimination	M_w (g mol^{-1})	M_n^a (g mol^{-1})	M_n^b (g mol^{-1})	Yield (%)
1	Nil	13430	4180	4380	93
2	Vacuum (10 mbar)	32010	13920	13690	90
3	N_2 (500 ml min^{-1})	32250	15090	12670	83

[a] Values from SEC in CH_2Cl_2. [b] Values from ^1H NMR ($CDCl_3$).

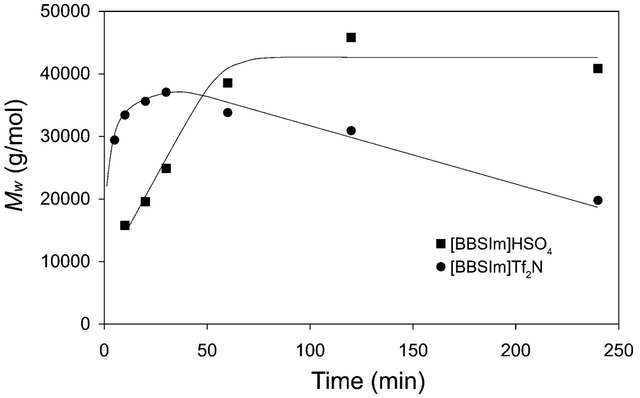
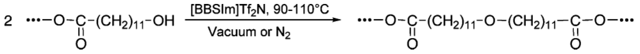


Fig. 3 Evolution of M_w during the polycondensation of 12-HDA in [BBSIm]HSO_4 and in [BBSIm]Tf_2N (12-HDA/BAIL molar ratio = 1/1, 110 °C, N_2).

However, as mentioned above, molar mass began decreasing in the former after 40 min while it kept growing before reaching a plateau at *ca.* 60 min in the latter.

At the beginning of reaction, kinetics is the determining factor and, since acid-catalyzed polyesterifications are second-order reactions, molar mass grows linearly with time.[43] As chain length keeps increasing, reaction medium viscosity increases and residual water cannot be totally removed. This prevents reversible polyesterification from completion and can explain why poly(12-HDA) stopped growing after 1 h in [BBSIm]HSO_4. However, the decrease of the molar mass of the polymer formed in [BBSIm]Tf_2N seemed rather surprising and led us to further investigations. The composition of each polymer was analyzed by ^1H NMR. It was found that one single reaction, *i.e.* esterification, occurred in [BBSIm]HSO_4. On the other hand, a side reaction, etherification, took place in [BBSIm]Tf_2N (Scheme 3), as reflected by the presence of H^h resonance at 3.38 ppm in the ^1H NMR spectrum of the corresponding polyester (Fig. 4).



$$2\ \cdots\!-\!O\!-\!\underset{\underset{O}{\|}}{C}\!-\!(CH_2)_{11}\!-\!OH \xrightarrow[\text{Vacuum or } N_2]{[\text{BBSIm}]\text{Tf}_2\text{N, 90-110°C}} \cdots\!-\!O\!-\!\underset{\underset{O}{\|}}{C}\!-\!(CH_2)_{11}\!-\!O\!-\!(CH_2)_{11}\!-\!\underset{\underset{O}{\|}}{C}\!-\!O\!-\!\cdots$$

Scheme 3 Etherification side-reaction in [BBSIm]Tf_2N.

Etherification is detrimental to polyester growth, as it consumes –OH end-groups, making the system no longer stoichiometric for polyesterification and, therefore, limiting polyester molar mass. As can be seen in Fig. 5, etherification took place in all the reactions conducted in [BBSIm]Tf_2N, reaching a plateau after 40 min reaction. Since 2 mol of –OH is consumed to form 1 mol of ether, at most 0.8% of the hydroxyl groups of starting 12-HDA was therefore consumed by etherification. Supposing that the rest of the –OH groups react totally as desired, the theoretical limiting value of the number-average degree of polymerization in this IL can be calculated to be DP_n = 249, which corresponds to a number-average molar mass of M_n = 49600 g mol^{-1} and, assuming an equilibrium polycondensation, a mass-average molar mass of M_w = 99200 g mol^{-1}. The maximal M_w that could be obtained in our investigations was around 40000 g mol^{-1}, which means that the reaction was far from its theoretical equilibrium.

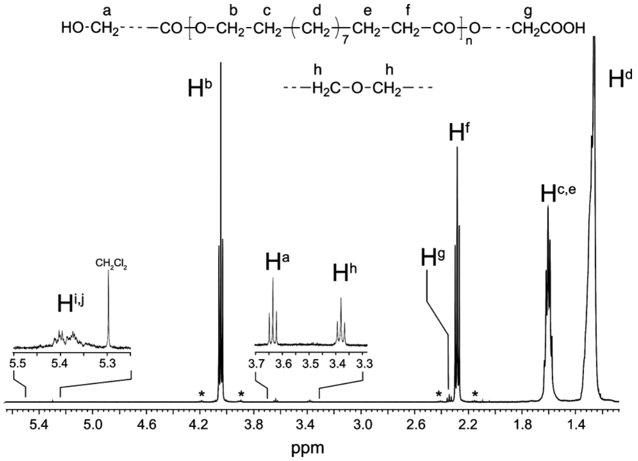


Fig. 4 ^1H NMR spectrum ($CDCl_3$, 500 MHz) of poly(12-HDA) synthesized in [BBSIm]TF_2N (110 °C, 1 h, N_2). *: ^{13}C satellite peaks. $H^{i,j}$: see text.

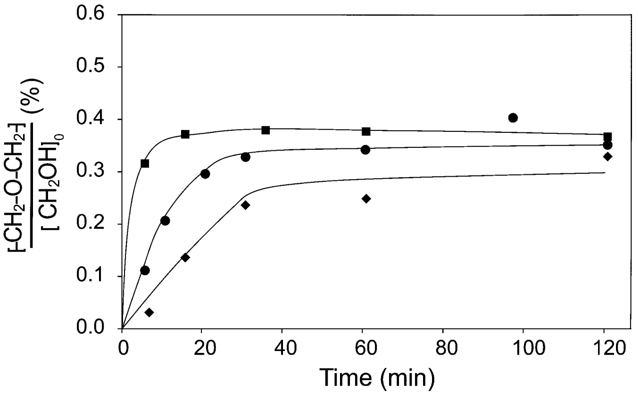
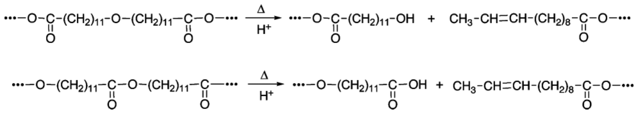


Fig. 5 Evolution of ether group content with time during 12-HDA polyesterification in [BBSIm]Tf_2N. (●): at 110 °C under N_2 flow, (■): at 110 °C under vacuum (10 mbar), (◆) at 90 °C under vacuum (10 mbar). Ether group content, determined by ^1H NMR, is expressed in mol-% with respect to initial OH groups.

The M_w decrease observed after 40 min reaction implies the existence of side-reactions other than etherification. The ^1H NMR spectra of the samples obtained in [BBSIm]Tf_2N present a resonance at 5.4 ppm (signal $H^{i,j}$) (Fig. 4) that reflects the presence of CH_3-CH═CH- double bonds in the polymer.

The formation of double bonds under acidic conditions is a known side-reaction during acid-catalyzed esterifications,[44,45] or during high temperature polyesterifications such as PET synthesis.[2] In the present case, the double bonds may result from acid-catalyzed scission of ester bonds, from acid-catalyzed scission of ether bonds formed by etherification or from acid-catalyzed hydroxy end-group dehydration. When a poly(12-HDA) synthesized in [BBSIm]HSO$_4$ was heated in [BBSIm]Tf$_2$N for 4 h, its M_w decreased from 41500 g mol^{-1} to 26270 g mol^{-1}. Since this polymer does not contain any ether groups, it can only be due to ester scissions. On the other hand, when a poly(12-HDA) synthesized in [BBSIm]Tf$_2$N was heated in [BBSIm]HSO$_4$ for 4 h, a slight M_w increase from 20350 g mol^{-1} to 26440 g mol^{-1} was observed. This indicates that poly(12-HDA) is stable in [BBSIm]HSO$_4$, while ester scission takes place in [BBSIm]Tf$_2$N when the reaction is prolonged (Scheme 4). It is important to note that etherification side-reaction was always observed during polyesterifications in [BBSIm]Tf$_2$N. Therefore, ether scissions (Scheme 4) might also participate in the M_w decrease observed at long reaction times for polyesterifications in this BAIL. Neither ethers nor double bonds were found in the samples obtained by reactions in [BBSIm]HSO$_4$, highlighting the specific role of Tf$_2$N$^-$ counterion in the side reactions.



Scheme 4 Formation of double bonds by ester (top) and ether (bottom) scission.

In order to get more information about the different behaviors of these two BAILS as solvent/catalyst for polyesterification, model reactions with dodecanoic acid and dodecan-1-ol were carried out: dodecanoic acid was added respectively in [BBSIm]HSO$_4$ and [BBSIm]Tf$_2$N, and the mixtures were heated at 110 °C overnight. No reaction was observed in either of them. The same test was subsequently conducted between dodecan-1-ol and the two BAILs. Dodecan-1-ol reacted with [BBSIm]HSO$_4$, since the reaction medium became rapidly (5 min) soluble in chloroform while [BBSIm]HSO$_4$ is insoluble. The ^{1}H NMR spectrum of the reaction product (Fig. 6) exhibits a new resonance at 4.04 ppm that can be assigned to the -SO$_3$-CH$_2$- sulfonate ester group (H^{12}).[46] This means that the dodecyl sulfonate ester of [BBSIm] cation has been formed. The structure of this compound was confirmed by ESI mass spectrometry, since a cation of the expected formula ($C_{23}H_{45}N_2O_3S^+$, 429.31 *m/z*) was detected as the main compound. On the other hand, no sulfonate dodecyl ester was detected in [BBSIm]Tf$_2$N.

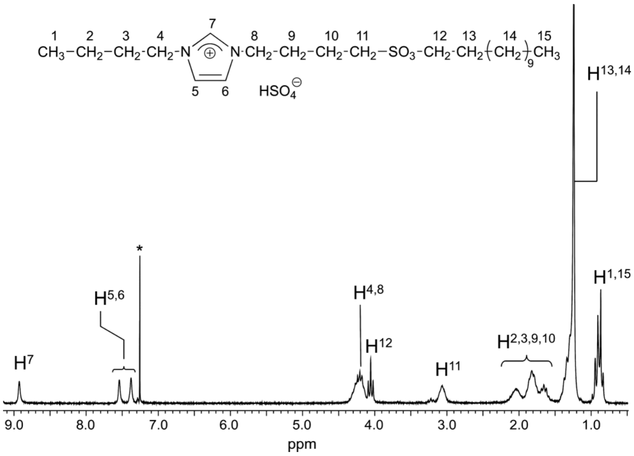


Fig. 6 ^{1}H NMR spectra (200 MHz, CDCl$_3$) of the product of reaction between 1-dodecanol and [BBSIm]HSO$_4$. *: signal of CHCl$_3$.

When dodecanoic acid was introduced in the reaction medium after the formation of the dodecyl sulfonate ester and the medium maintained under the same conditions, a phase separation was observed. The ^{1}H NMR study showed that the upper phase mainly contained dodecyl dodecanoate (Fig. 7), while only [BBSIm]HSO$_4$ was found in the lower phase. This shows that the dodecyl sulfonate ester reacts with carboxylic acids and can be regarded as a reaction intermediate.

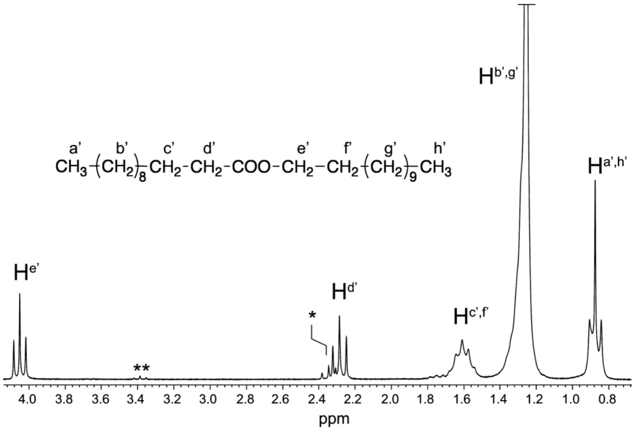
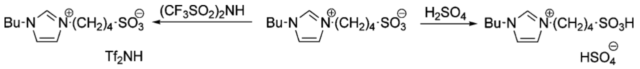


Fig. 7 Reaction between the [BBSIm]HSO$_4$ sulfonate dodecyl ester and dodecanoic acid (110 °C): ^{1}H NMR spectra (in CDCl$_3$) of the upper phase of reaction medium. *: residual dodecanoic acid. ** traces of ether groups.

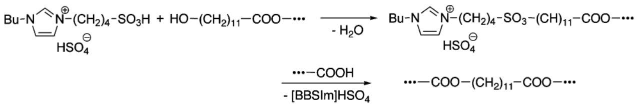
It turned out that the behavior of the two BAILs was completely different, and it made us doubt if they had the same chemical structure, as assumed in Scheme 1. $(CF_3SO_2)_2NH$ is a moderately strong acid with a pK_a value of 1.7,[47] while H_2SO_4 and sulfonic acid are very strong acids with negative pK_a values.[48,49] The Hammet acidity function H_0 can be used to compare their acidities.[50] The H_0 value of H_2SO_4 is –12,[51] while H_0 values of sulfonic acids range from –5.8 to –7.9.[52–54] This indicates that acidities are in the order H_2SO_4 > sulfonic acid ≫ $(CF_3SO_2)_2NH$. It can therefore be predicted that the acidity of the sulfonic acid group of [BBSIm] cation is higher than that of $(CF_3SO_2)_2NH$ but lower than that of H_2SO_4. Consequently, when the BBSIm zwitterion is mixed with sulfuric acid, the sulfonate ion–sulfonic acid equilibrium is shifted towards sulfonic acid. On the other hand, when BBSIm zwitterion is mixed with Tf$_2$NH, sulfonic acid cannot be formed, as a stronger acid cannot be produced from a weaker one. [BBSIm]Tf$_2$N, should, therefore, be considered as a mixture of zwitterion and Tf$_2$NH, interacting through *e.g.* hydrogen bonds,[55] rather than as a ionic liquid with separate anion and cation (Scheme 5).

Sulfonate ester can be formed in [BBSIm]HSO$_4$, but not in [BBSIm]Tf$_2$N since -SO$_3^-$ cannot react with –OH groups. The formation of the sulfonate ester in [BBSIm]HSO$_4$ competes with both etherification side reaction and esterification main reaction.



Scheme 5 Reactions between BBSIm zwitterion and H_2SO_4 or Tf_2NH.

It reduces the concentration of –OH groups (etherification reactant) and that of $–SO_3H$ (etherification catalyst), and, therefore, limits the extent of the etherification reaction. At latter stages of the reaction, –COOH groups can react with the sulfonate ester, yielding the expected carboxylate ester. This reaction (Scheme 6) could explain why no etherification was observed in $[BBSIm]HSO_4$.



Scheme 6 Polyesterification of 12-HDA in $[BBSIm]HSO_4$ through the sulfonate ester pathway.

Different concentration of BAILs

In order to check the influence of BAIL concentration on polyesterification, a series of experiments were carried out using 1-butyl-3-methylimidazolium hydrogen sulfate or bis(trifluoromethylsulfonyl)imidide ($[BMIm]HSO_4$ or $[BMIm]Tf_2N$, respectively), or 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imidide ($[OMIm]Tf_2N$) as diluents (Table 4). The BAIL mol ratio in each BAIL/IL mixture varied from 1.0 to a low level (0.01).

Reactions were first conducted in $[BBSIm]Tf_2N/[BMIm]Tf_2N$ mixtures and it turned out that diluting $[BBSIm]Tf_2N$ in $[BMIm]Tf_2N$ did not affect the polymer molar mass much after 30 min reaction, the maximum being obtained at 0.5 mol ratio of $[BBSIm]Tf_2N$. At 0.1 mol ratio, catalysis was still effective and even better than in pure $[BBSIm]Tf_2N$. However, molar mass decreased dramatically when $[BBSIm]Tf_2N$ mol ratio was reduced to 0.01 and the catalyst concentration was not sufficient any more to accelerate the polyesterification. The same experiments were also carried out in mixtures of $[OBSIm]Tf_2N$ and $[OMIm]Tf_2N$, but the molar masses of resulting polyesters were lower, comparing to that obtained with their butyl-substituted homologue and decreased continuously as $[OBSIm]Tf_2N$ concentration decreased. The same trend was observed in $[BBSIm]HSO_4$ (Table 4).

It is worth emphasizing that less ether was formed when the BAIL concentration decreased. This might be another reason why higher molar mass polyesters were obtained in BAIL/IL 50/50 mol mixture, since fewer hydroxyl groups were consumed by this side reaction.

Conclusion

The polyesterification of 12-HDA in various BAILs has been studied and found to be very efficient, since high molar mass polyesters (M_w of *ca.* 40000) were obtained at much lower temperature and shorter reaction time than conventional polyesterifications: 15–30 min at 90–110 °C *versus* several hours at 170–300 °C. However, there are some noticeable differences between the different BAILs studied. In $[BBSIm]HSO_4$ only the desired polyesterification was observed and a M_w plateau was reached after 60 min reaction. On the other hand, the reaction was much faster in $[BBSIm]Tf_2N$, as M_w close to 35000 g mol^{-1} were obtained after only 5 min reaction, but the side reactions took place, *i.e.* etherification of OH end-groups and degradation leading to significant molar mass decrease at long reaction time. This degradation was assigned to acid-catalyzed ester scissions with formation of double bonds and carboxylic acids. However, it should be mentioned that ether scissions might also be involved in the degradation.

The different behaviors of these BAILs in polyesterification were investigated using dodecanoic acid and dodecan-1-ol as model compounds. Dodecan-1-ol was found to react with $[BBSIm]HSO_4$, yielding the sulfonic acid dodecyl ester of BBSIm cation, while it did not react with $[BBSIm]Tf_2N$. The sulfonate ester was found in turn to react with dodecanoic acid, leading to dodecyl dodecanoate. From these experiments, it can be inferred that, during polyesterification in $[BBSIm]HSO_4$, the formation of sulfonate ester intermediate protects –OH groups against etherification side reaction, but still allows the formation of the expected polyester by reaction with carboxylic acids.

Table 4 Polyesterification of 12-HDA carried out in BAIL/IL mixtures at 110 °C for 30 min under N_2 (500 ml min^{-1}): number-average and weight-average molar masses (M_n and M_w) of resulting polyesters determined by SEC and NMR

Entry	BAIL	IL	$\frac{[BAIL]}{[BAIL]+[IL]}$	M_n (SEC)	M_w (SEC)	M_n (NMR)	Eher[a] (mol-%)
1	$[BBSIm]Tf_2N$	$[BMIm]Tf_2N$	1.00	17960	37070	11780	0.33
2	$[BBSIm]Tf_2N$	$[BMIm]Tf_2N$	0.75	22840	40420	18360	0.28
3	$[BBSIm]Tf_2N$	$[BMIm]Tf_2N$	0.50	24020	44190	18970	0.29
4	$[BBSIm]Tf_2N$	$[BMIm]Tf_2N$	0.10	21240	44740	14660	0.22
5	$[BBSIm]Tf_2N$	$[BMIm]Tf_2N$	0.01	1370	3200	1530	0.00
6	$[OBSIm]Tf_2N$	$[OMIm]Tf_2N$	1.00	14580	36110	15680	0.65
7	$[OBSIm]Tf_2N$	$[OMIm]Tf_2N$	0.75	10430	32160	8200	0.60
8	$[OBSIm]Tf_2N$	$[OMIm]Tf_2N$	0.50	9830	29270	10650	0.50
9	$[OBSIm]Tf_2N$	$[OMIm]Tf_2N$	0.10	7390	26070	7880	0.30
10	$[OBSIm]Tf_2N$	$[OMIm]Tf_2N$	0.01	630	1610	1080	0.00
11	$[BBSIm]HSO_4$	$[BMIm]HSO_4$	1.00	10310	24910	10140	0.00
12	$[BBSIm]HSO_4$	$[BMIm]HSO_4$	0.50	7750	19940	5100	0.00
13	$[BBSIm]HSO_4$	$[BMIm]HSO_4$	0.10	950	2543	2410	0.00

[a] $-CH_2$-*O*-CH_2- mol-% with respect to initial $–H_2OH$ groups determined by ^1H NMR.

To explain the differences between these two BAILs, and considering the stronger acidity of H_2SO_4 with respect to that of Tf_2NH, we suggest that [BBSIm]HSO_4 could be composed of an imidazolium-based sulfonic acid and its counterion HSO_4^-, while [BBSIm]Tf_2N could consist of a mixture of imidazolium-based sulfonate zwitterion and proton donor Tf_2NH.

Several reaction conditions were tested. It was, of course, necessary to remove water from the reaction medium to obtain polyesters, but high molar mass polymers were obtained when the reaction was carried out either under moderate vacuum (10 mbar) or under nitrogen flow (500 ml min^{-1}), even though vacuum led to slightly higher molar masses. Increasing the reaction temperature increased the reaction rate, but had little influence on the maximum molar masses. The paper also confirms that the length of the alkyl group of imidazolium cation and the counterion have an important impact on BAIL dissolving abilities. However, the solubility of reactants is not necessarily critical to their reactivity, since high molar mass polymers were obtained in [BBSIm]HSO_4 and [BBSIm]Tf_2N, in which large molten polymer particles (200 μm) formed during the reaction, as well as in [OBSIm]Tf_2N, in which the polymer was soluble. Moreover, polymer separation could be facilitated by their insolubility in BAILs.

Polyesterification was also conducted in dilute BAIL/IL mixtures. Polyesters of lower molar masses were obtained after 30 min reaction when the BAIL concentration decreased, except for [BBSIm]Tf_2N, which was still efficient at 1/10 mol dilution in neutral [BMIm]Tf_2N. This may be connected to the very high reaction rate in this BAIL, where maximum molar mass is reached after only 5 min reaction. At 1/10 dilution, 30 min reaction time appears to be enough to reach maximum molar mass.

Even though the reaction is faster and the reaction medium is much less viscous in Tf_2N-based BAILs than in HSO_4-based ones, the latter appears more suited to the synthesis of well-defined polyesters, without side reactions.

Preliminary studies on the recycling of [BBSIm]HSO_4 after polymer separation showed that catalytic activity remained the same after 4 runs. Further studies will be carried out to find out if catalytic activity remains unchanged for the other BAILs used in our study. Further studies are also needed to improve the polymer separation method, which could be a simple filtration of the viscous reaction medium or precipitation in water. Microwave heating could also be used to further reduce the reaction time.[8,9]

Experimental

Chemicals

1-Butylimidazole (Aldrich, 98%), 1-octylimidazole (Iolitec, >99%), 1,4-butane sultone (Aldrich, >99%), concentrated sulfuric acid (Aldrich, 96%), bis(trifluoromethylsulfonyl)imide (Iolitec, 99%, in 80% aqueous solution), dodecan-1-ol (Fluka, >99.5%), dodecanoic acid (Aldrich, >99%), 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIm]HSO_4, Solvionic >98%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imidide ([BMIm]Tf_2N, Solvionic >99.5%) and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imidide ([OMIm]Tf_2N, Solvionic > 99.5%) were used as received. 12-Hydroxydodecanoic acid (Aldrich, 97%) was dried under vacuum to eliminate residual solvent prior to use.

Synthesis of BAILs

4-(3′-Butyl-1′-imidazolio)-1-butanesulfonic acid hydrogen sulfate ([BBSIm]HSO_4), 4-(3′-butyl-1′-imidazolio)-1-butanesulfonic acid bis(trifluoromethylsulfonyl)imidide ([BBSIm]Tf_2N), and 4-(3′-octyl-1′-imidazolio)-1-butanesulfonic acid bis(trifluoromethylsulfonyl)imidide ([OBSIm]Tf_2N) were synthesized according to known procedures,[28,30] by reacting 1,4-butane sultone with 1-alkylimidazole and converting the resulting zwitterions to the corresponding BAILs by acidification with equimolar amount of sulfuric acid or bis(trifluoromethylsulfonyl)imide. The BAILs were dried under vacuum at 40 °C overnight. The water content of dried BAILs, measured by KF titration, was 0.49, 0.65 and 0.39 wt-% for [BBSIm]Tf_2N, [BBSIm]HSO_4 and [OBSIm]Tf_2N, respectively.

Polycondensation of 12-hydroxydodecanoic acid

In each experiment, 1 mmol (0.2630 g) of 12-hydroxydodecanoic acid was mixed with 1 mmol of BAIL in a glass tube fitted with a nitrogen inlet and outlet and a magnetic stirring bar. The reaction was carried out at 90 or 110 °C for a predetermined time under nitrogen flow (500 mL min^{-1}) or under vacuum (10 mbar) to eliminate reaction water. At the end of the reaction, 10 mL of isopropanol was added and the mixture heated under reflux for 10 min. The resulting suspension was cooled down to room temperature and the precipitate was filtrated, washed two times with 10 ml of isopropanol, then 3 times with 5 ml of diethyl ether. The polyester was then dried at 40 °C overnight under vacuum (10 mbar).

Reaction between dodecan-1-ol and [BBSIm]HSO_4

1 mmol (0.3581 g) of [BBSIm]HSO_4 was mixed with 1 mmol (0.1863 g) of dodecan-1-ol in a glass tube equipped with a nitrogen inlet and outlet and a magnetic stirring bar. The reaction was conducted at 110 °C for 30 min under nitrogen flow (500 mL min^{-1}) to strip water. The reaction product was analyzed by NMR and mass spectrometry as discussed in the text.

Analytical Methods

NMR Spectroscopy: ^1H NMR spectra of the monomer and polymers were recorded on a Bruker Avance 200 and 500 spectrometers in chloroform-*d* (ref. $\delta_H(CHCl_3) = 7.26$ ppm).

Steric Exclusion Chromatography (SEC): The SEC equipment consisted of a Waters 515 HPLC pump, a Waters 410 refractive index detector and a set of five Ultrastyragel columns ($50 + 500 + 10^3 + 10^4 + 10^5$ Å). CH_2Cl_2 was used as eluting solvent with a flow rate of 1 ml/min. Each sample was prepared with 8 mg of polymer, 1 ml of CH_2Cl_2 and 1 μl of toluene. For each analysis, 100 μl of sample was injected. All the analyses were carried out at room temperature. Polystyrene standards were used to calibrate the system.

Polarizing optical microscopy (POM): The polymerizations of 12-hydroxydodecanoic acid in BAILs (1/1 mol) were followed under a Leica DM2500 polarizing optical microscopy equipped with a camera. The temperature was programmed as follows: heating from 20 °C to 110 °C with a heating rate of 20 °C min^{-1}, holding for 5 min at 110 °C, then cooling down to 20 °C with a cooling rate of 20 °C/min.

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