



Cite this: *RSC Adv.*, 2020, **10**, 35381

A non-metal route to realize the bio-based polyester of poly(hexylene succinate): preparation conditions, side-reactions and mechanism in sulfonic acid-functionalized Brønsted acidic ionic liquids†

Chenyang Wei,^a Zhengping Liu, ^{*a} Hongwei Tan, ^b Liyan Huang ^a and Jun Li^a

Received 20th August 2020
 Accepted 16th September 2020
 DOI: 10.1039/d0ra07157a
rsc.li/rsc-advances

A biodegradable linear bio-based polyester of poly(hexylene succinate) was effectively prepared in non-metal sulfonic acid-functionalized Brønsted acidic ionic liquids (SFBAILs) as both the catalyst and the polymerization medium, and the processes of polycondensation and post-polycondensation in SFBAILs were also investigated. In addition, the side reactions which were detrimental to the growth of M_w of poly(hexylene succinate) were evaluated and the synthesis mechanism of poly(hexylene succinate) catalyzed by SFBAILs was discussed with the help of DFT calculations. The result shows that both the imidazole ring and the sulfonic group on cations of SFBAILs play an important role in the catalytic process.

Introduction

Biomass is one of the largest quantities of natural resources in the world, and every year 104.9 petagrams of carbon biomass is produced.¹ Biomass derived from agricultural residues and forest by-products has both easy processability and relatively low cost.² Thus, biomass can be called a “green resource”, and fits well with the concept “sustainable development”, *i.e.*, “sustainable development is a social development which fulfils the needs of present generations without endangering the possibilities of fulfilment of the needs of future generations”.³ However, this material is not fully utilized and a large quantity of biomass is simply burned and causes pollution every year.

To solve this problem, a new material, biomass polyesters, has been formed. Polyesters formed by biomass are among the most promising polymers. Polyesters are usually biodegradable and biocompatible, and the monomers from biomass are easily accessed. Moreover, different monomers with different structures and properties makes polyesters have a wide range of applications.⁴ Due to their multiple properties, polyesters formed by biomass become a research focus of green chemistry. The synthesis of polyesters is usually realized by polycondensation.

However, polycondensation generally requires harsh conditions. A high temperature (160–300 °C) and vacuum are applied at polycondensation to remove small molecules from the polymerization systems and obtain a relatively high molecular weight. This traditional method is usually limited by low heat transfer efficiency caused by viscous reaction systems and side reactions due to the high temperature. The catalyst is also a considerable aspect of the polycondensation due to the long reaction time (more than several hours). However, most recent studies focused on metal catalysts, such as metal salts, metal oxides or metal alkoxides, in particular, catalysts based on Sn or Zn and metals inevitably remain in the products, limiting the use of products.⁵ In Yoon’s work, high molecular weight poly(*L*-lactic acid) was obtained by Ti(OBu)₄. Although 130 kDa of molecular weight could be achieved, the use of metal catalysis is a necessary.⁶ The method of solution reaction is also mentioned in Fradet’s work as a resolution for low molecular weight caused by traditional methods,⁷ but the expensive or toxic starting monomers, activating agents and solvents limit the method. In addition, with the higher standard of environmentally friendliness, using fewer organic solvents or recyclable solvents is necessary due to a large amount of waste during the process of producing polymers.⁸

Considering these problems, there has recently been growing interest in ionic liquids, which were applied to synthesize polymers such as polyimide, polyamide,⁹ polysulfone,¹⁰ and polyester,¹¹ or copolymers such as polyesteramide.¹² Brønsted acidic ionic liquids (BAILs) are ones with task-specific functionality and well known in polymers synthesis for its remarkable ability of catalysis.¹³ A simple route can be used to separate BAILs from the products. Moreover,

^aBNU Key Lab of Environmentally Friendly and Functional Polymer Materials, Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China. E-mail: lzp@bnu.edu.cn; Fax: +86 10 58802075; Tel: +86-10-58806896

^bBNU Institute of Theoretical and Physical Chemistry, College of Chemistry, Beijing Normal University, Beijing 100875, China

† Electronic supplementary information (ESI) available: UV-vis spectra and DFT calculations results. See DOI: 10.1039/d0ra07157a



BAILS have the properties of conventional ionic liquids such as non-volatility, non-flammability, a wide liquidus range and high conductivity. With so many advantages, they are being used in many fields.¹⁴

In Fradet's works,¹⁵ some types of polyesters (mainly linear polyesters of 12-hydroxydodecanoic acid hyperbranched polyester of 2,2-bis(hydroxymethyl)propanoic acid) were produced in two types of Brönsted acidic ionic liquids, that is, HSO_4^- anionic and Tf_2N^- anionic BAILS, in a relatively mild reaction condition. In our recent work,¹⁶ the high molecular weight copolymer of L-lactic acid and ϵ -caprolactone were achieved in SFBAILS in a mild condition. Thus, Brönsted acidic ionic liquids are potentially selected for polycondensation.

Poly(hexylene succinate) is a type of novel and promising polyester plasticizer for the modification of poly(vinyl chloride) (PVC) and can be employed as an alternative of the traditional dioctyl phthalate (DOP).¹⁷ However, few investigations concentrated on this polyester synthesized in BAILS. And not only that, the side reactions which usually happen in the post-polycondensation process limit the growth of M_w of this product and restrict the further practical applications. Therefore, it is necessary to study the side reactions in this process.

In this report, we investigated the polycondensation and post-polycondensation process of linear monomers of succinic acid and 1,6-hexanediol in sulfonic acid-functionalized Brönsted acidic ionic liquids (SFBAILS), which belong to a Brönsted acidic ionic liquids and are known for their catalytic capability. And the most suitable reaction condition was explored. Moreover, the side reactions during the post-polycondensation in SFBAILS were discussed, and an interesting paradox between our observations and the theory proposed by Fradet *et al.* was witnessed. To explain this phenomenon, density functional theory (DFT) calculations were firstly carried out here and an explanation for this paradox was worked out, which refined this already existed theory. Moreover, with the help of DFT method, a simple but reasonable model was established and the catalytic mechanism of SFBAILS was revealed.

Results and discussion

In this work, six sulfonic acid-functionalized Brönsted acidic ionic liquids (SFBAILS) with different cations and anions were synthesized and were used as catalysts and media. The polycondensation and post-polycondensation processes of oligo(hexylene succinate) were investigated in these SFBAILS (Table 1).

Acidity of SFBAILS

Herein, the Hammett acidity functions (H_0) were used to evaluate the acidity of SFBAILS by UV-vis spectroscopy. The results are listed in ESI (Fig. S1, S2 and Table S1).[†]

Hammett acidity function is defined as¹⁹

$$H_0 = \text{p}K(\text{I})_{\text{aq}} + \log\left(\frac{[\text{I}]}{[\text{IH}^+]}\right)$$

Table 1 H_0 values of SFBAILS determined by UV-vis spectroscopy at 50 °C

SFBAILS	Cations	Anions	H_0^a
$[\text{BSMIM}]^+[\text{HSO}_4^-]$		HSO_4^-	-3.34
$[\text{BSMIM}]^+[\text{TFS}]$		CF_3SO_3^-	-4.06
$[\text{BSMIM}]^+[\text{TS}]$		$p\text{-CH}_3(\text{C}_6\text{H}_4)\text{SO}_3^-$	-3.50
$[\text{BSMIM}]^+[\text{MS}]$		CH_3SO_3^-	-3.34
$[\text{BSMIM}]^+[\text{BF}_4^-]$		BF_4^-	-3.68
$[\text{BSPy}]^+[\text{HSO}_4^-]$		HSO_4^-	-3.30 ^b

^a The Hammett acidities of SFBAILS were determined using the Hammett method with UV-vis spectroscopy at 50 °C, and 25 mg L⁻¹ of 2,4-dichloro-6-nitroaniline were used as the indicator. ^b From ref. 18.

Here, $\text{p}K(\text{I})_{\text{aq}}$ is the $\text{p}K_a$ value of the aqueous solution of the indicator, and the $\text{p}K_a$ value of the indicator 2,4-dichloro-6-nitroaniline here is -3.31. $[\text{IH}^+]$ is the molar concentration of indicator protonated by SFBAILS and $[\text{I}]$ is the molar concentration of the unprotonated indicator.

As shown in Table 1, the acidities of SFBAILS determined by the Hammett method here range from -3.34 to -4.06, which has no difference from that of pyridinium-type sulfonic acidic ionic liquids according to the literature.

In our previous work, the acidities of SFBAILS were compared with the acidities of corresponding conventional organic sulfonic ionic liquids. We found that the order of SFBAILS acidity was related to the acidity of proton acid corresponding to the anions of SFBAILS, which may be due to the combination of concentrated anions of SFBAILS with protons. The stronger cohesiveness of anions and protons corresponds to the lower concentration of free hydrogen ions, and lower acidity (Scheme 1). However, anions hardly affect on the acidity of SFBAILS, because all of them have identical sulfonic acid group and acidity.

Thermal stability of SFBAILS

The thermal stability of SFBAILS is very important because the post-polycondensation usually requires a relatively high polymerization temperature. Most of the SFBAILS have excellent thermostability, and their decomposition temperatures are higher than 250 °C. However, $[\text{BSMIM}]^+[\text{BF}_4^-]$ shows a different decomposition process. There are two decomposition stages at approximately 110 °C and 310 °C. The weight loss between two stages is approximately 20%, which can be attribute to the weight loss of BF_3 due to the conversion of $[\text{BSMIM}]^+[\text{BF}_4^-]$ to $[\text{BSMIM}]^+[\text{F}]$ (Fig. 1).



Scheme 1 Dissociation equilibrium of sulfonic acid-functionalized Brönsted acidic ionic liquids.



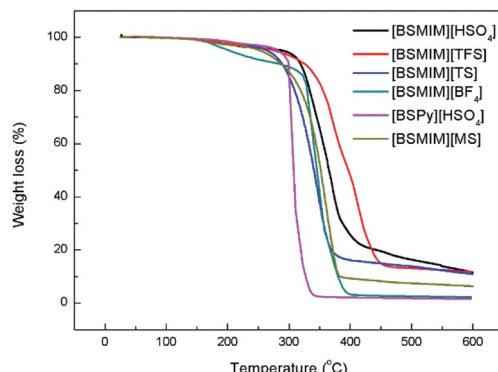


Fig. 1 Thermogravimetric curves of different sulfonic acid-functionalized Brønsted acidic ionic liquids.

Post-polycondensation in SFBAILS

Miscellaneous post-polycondensation conditions in SFBAILS were investigated in this work. Table 2 shows that the type of anions and cations has no effect on the molecular weight of polymers in this system. The molecular weight of polymer in $[\text{BSMIM}][\text{HSO}_4]$ can reach 22 kDa, which is the highest. The molecular weight of polymer in $[\text{BSMIM}][\text{BF}_4]$ is minimum, which can be explained by the decomposition of $[\text{BSMIM}][\text{BF}_4]$ determined by the analysis of thermal stability.

Furthermore, the different polymerization temperature was studied. The most suitable temperature is 110 °C, followed by 100 °C, and 120 °C is the least. This result is attributed to the fact that a lower temperature can contribute to a lower reaction rate while a higher temperature can generate more side reactions.

Moreover, experiments in different methods of water removal were conducted to evaluate the most effective method

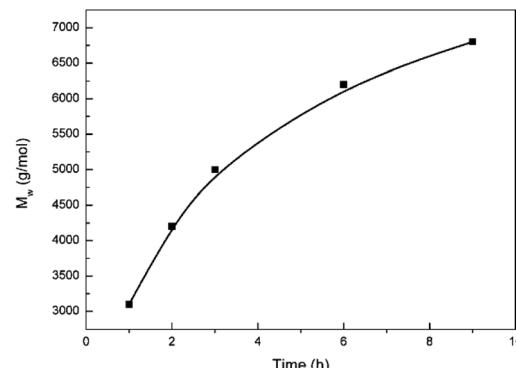


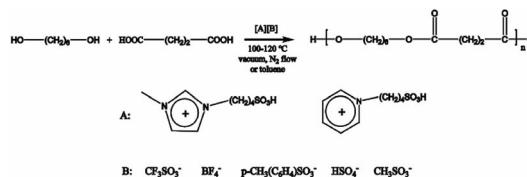
Fig. 2 M_w of oligo(hexylene succinate) with reaction time.

to remove water. Clearly, the effective method is blowing nitrogen. The vacuum degree in the vacuum system is an important aspect of affecting the molecular weight of polymer. When the system reaches 2000 Pa, the water in this system can hardly be moved. However, when the system reaches 1000 Pa, the water can be relatively effectively removed. In our previous work,²⁰ toluene was used to eliminate water since the formation of azeotrope between water and toluene can help water remove in reaction system. However toluene to remove water does not appear effective due to the low temperature that cannot help the azeotrope of water and toluene to effectively evaporate.

Dynamics of the polycondensation and post-polycondensation in SFBAILS

The polycondensation process. The polycondensation process was monitored by the SEC method and the molecular weights of oligomers with different reaction times were

Table 2 Post-polycondensation of oligo(hexylene succinate) in sulfonic acid-functionalized Brønsted acidic ionic liquids^a



Run	SFBAILS	Temp. (°C)	Water removal ^b	M_w (kDa)	PDI	Yield (%)
1	$[\text{BSMIM}][\text{HSO}_4]$	110	N_2 -flow	22.0	1.78	80.1
2	$[\text{BSMIM}][\text{TFS}]$	110	N_2 -flow	22.0	1.79	76.5
3	$[\text{BSMIM}][\text{TS}]$	110	N_2 -flow	15.0	1.56	81.2
4	$[\text{BSMIM}][\text{MS}]$	110	N_2 -flow	15.1	1.63	66.3
5	$[\text{BSMIM}][\text{BF}_4]$	110	N_2 -flow	9.9	1.50	52.4
6	$[\text{BSPy}][\text{HSO}_4]$	110	N_2 -flow	12.7	1.60	78.7
7	$[\text{BSMIM}][\text{HSO}_4]$	110	Toluene	10.4	1.75	76.2
8	$[\text{BSMIM}][\text{HSO}_4]$	110	2000 Pa	7.3	1.57	77.3
9	$[\text{BSMIM}][\text{HSO}_4]$	110	1000 Pa	12.8	1.64	79.2
10	$[\text{BSMIM}][\text{HSO}_4]$	100	N_2 -flow	14.3	1.59	69.8
11	$[\text{BSMIM}][\text{HSO}_4]$	120	N_2 -flow	13.9	1.62	65.1

^a Post-polycondensation: post-polycondensation at the given temperature for 60 min. ^b In the nitrogen flow systems, flow rate of 500 mL min⁻¹ applied over the reaction.



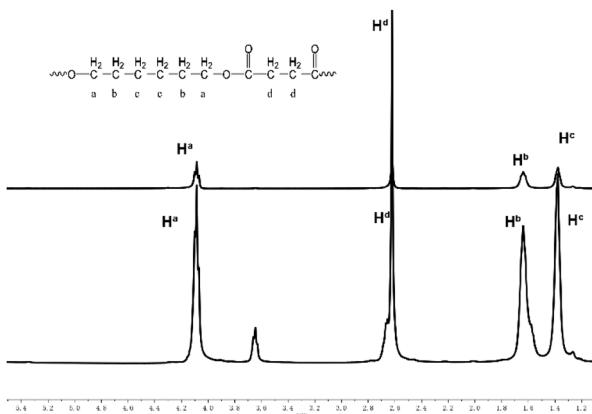


Fig. 3 ^1H NMR spectra (CDCl_3 , 400 MHz) of oligo(hexylene succinate) at the 2nd hour (below) and poly(hexylene succinate) at the 30th minute (above).

measured. The results are shown in Fig. 2. The results indicate that the molecular weights of oligomers increase with the reaction time in 9 h. However, the growth rate of oligomer's molecular weight decreases. For further research on this process, ^1H NMR was used to evaluate the kinetics. The oligomers were dissolved in CDCl_3 . Fig. 3 shows the ^1H NMR spectra of the oligomer and polymer of succinic acid and 1,6-hexanediol at different times.

Herein, P is used and defined as the conversion ratio, and P can be calculated by the concentration of the reactive functional group $-\text{OH}$. Thus, P can be defined as

$$P = ([\text{OH}]_0 - [\text{OH}]_t)/[\text{OH}]_0$$

The concentration of the reactive functional group -OH can be found from ^1H NMR spectra according to different chemical shifts between the main chains and the end groups.

In addition, the self-catalytic esterification usually applies to the third-order reaction model. The third-order rate equation can be defined as

$$1/(1 - P)^2 = kt + \text{Con.}$$

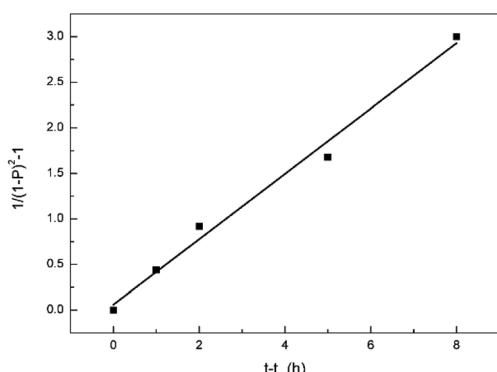


Fig. 4 Variation of $(1/(1 - p)^2 - 1)$ versus reaction time ($t - t_0$) of copolymerization of succinic acid and 1,6-hexamethylene glycol

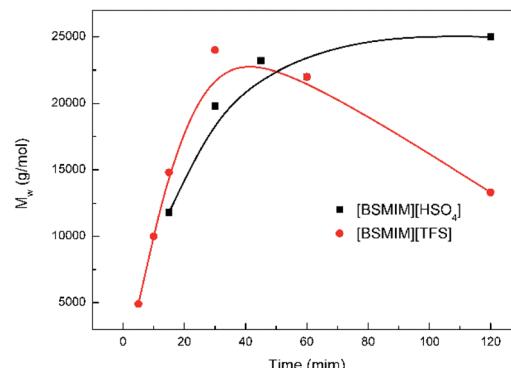


Fig. 5 M_w of poly(hexylene succinate) in [BSMIM][TFS] and [BSMIM][HSO₄]⁻ at different times

The results were shown in Fig. 4, and it has a good linear fitting, which implies that the third-order reaction model can be used to describe the polycondensation process. The main reason for the decrease in the molecular weight growth rate is the reaction consumption of acid instead of the system viscosity at 160 °C. In fact, at this temperature, the reaction system can still be easily magnetically stirred, which proves a relatively low viscosity during this process.

The study of post-polycondensation process. The post-polycondensation process in [BSMIM][HSO₄] and [BSMIM][TFS] were examined and the results were shown in Fig. 5. The results indicate that at the beginning of the reaction, the molecular weight of polymer quickly increases in both SFBAILS. However, a decrease in molecular weight can be observed after 30 min in [BSMIM][TFS]. At the beginning of the reaction, the growth rate of M_w fits well with linear since acid-catalyzed polyesterifications are second-order reactions.²¹ However, after 30 min, the polymerization medium viscosity increases, and water in this system cannot be easily moved, which, limits the molecular weight growth of polymers in SFBAILS. In fact, at 110 °C, the reaction medium was more viscous than that at 160 °C, which can explain this limitation. And a decrease was observed in [BSMIM][TFS].

For more information about this polymerization in SFBAILS, the decrease in molecular weight of polymer in SFBAILS was

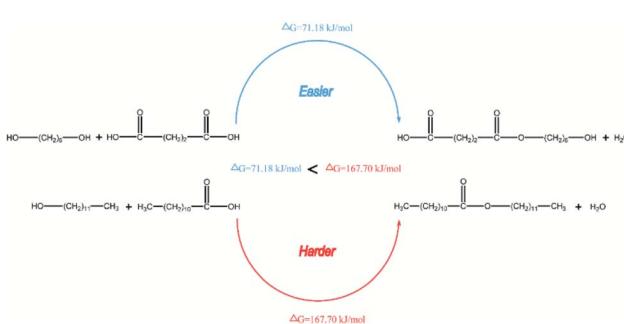


Fig. 6 The DFT calculations of free energies of two esterification processes

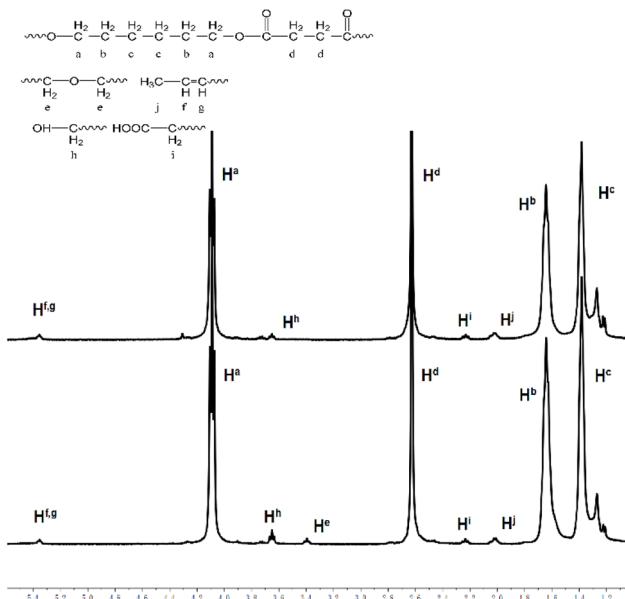
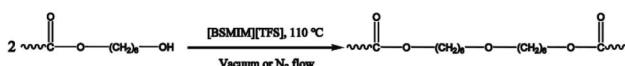


Fig. 7 ^1H NMR spectra (CDCl_3 , 400 MHz) of poly(hexylene succinate) catalysed by [BSMIM][TFS] (below) and by [BSMIM][HSO_4] (above).

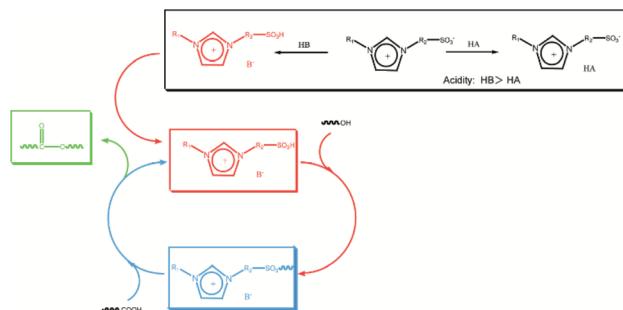
studied. Fig. 7 shows the ^1H NMR of polyesters catalyzed by [BSMIM][HSO_4] and [BSMIM][TFS], and Table 3 listed all the impurities. The resonance at 3.40 ppm, which proved another structure formed, is etherification, a well-known reaction happening between two OH-groups in the acidic environmental (Scheme 2). In fact, etherification can occur when aliphatic hydroxyl groups appear in SFBAILs.²² Etherification can consume $-\text{OH}$ end-groups and limit the polyesterification process, so the molecular weight decreases. However, this side reaction appears not to occur in [BSMIM][HSO_4]. In fact, in Fradet's case,²³ SFBAIL 3-butyl-1-(butyl-4'-sulfonic acid) imidazolium hydrogen sulfate ([BBSMIM][HSO_4]) can react with hydroxyl group of 12-hydroxydodecanoic acid (12-HDA) and sulfonic ester was formed (Scheme 3), then transesterification occurred between sulfonic ester and carboxylic acid. The

Table 3 The impurities examined by the ^1H NMR spectra of polyesters in [BSMIM][TFS] and [BSMIM][HSO_4]

Entry	Structure	Resonance
1	$\text{H}_3\text{C}-\text{C}=\text{C}\text{---}\text{C}\text{---}$ j f g	$\text{H}^{\text{f},\text{g}}$ (5.3–5.4 ppm) and H^{j} (1.8–2.2 ppm)
2	$\text{---}\text{C}\text{---}\text{O}\text{---}\text{C}\text{---}$ e e	H^{e} (3.2–3.4 ppm)



Scheme 2 Side reaction of etherification in [BSMIM][TFS] during the post-polycondensation process.



Scheme 3 Formation of sulfonic esters in SFBAILs.

concentration of hydroxyl group decreased, which limited the etherification process. If this theory is right, sulfonic esters can be formed between the hydroxyl groups and [BSMIM][HSO_4], demonstrating that the type of anions in SFBAILs are very essential in the behaviors of SFBAILs when they are used as the catalyst and the medium for polycondensation.

However, this theory seems inapplicable because ethers were found in polymer in [BSMIM][TFS] since $\text{CF}_3\text{SO}_3\text{H}$ is a relatively strong acid, [BSMIM][TFS] is formed by sulfonic acid and CF_3SO_3^- , sulfonic esters can be easily formed and no ethers should be observed. Therefore, further discussion is required. To obtain more information about the reaction, simple DFT calculations were conducted here at the method of B3LYP/def2svp in Gaussian 16 software to evaluate the difference of kinetics of these two reactions and the results were listed in Fig. 8, and all energies given here were the sum of electronic and thermal free energies at 110 °C. Grimme's empirical dispersion-correction and solvation effects (using the PCM model with dichloroethane as the solvent²⁴) were introduced to all calculations, optimization and frequency analysis. As indicated before, the routes proposed by Fradet's work went through two competitive experiments: one is the formation of sulfonate esters and the other is the main reaction, and more

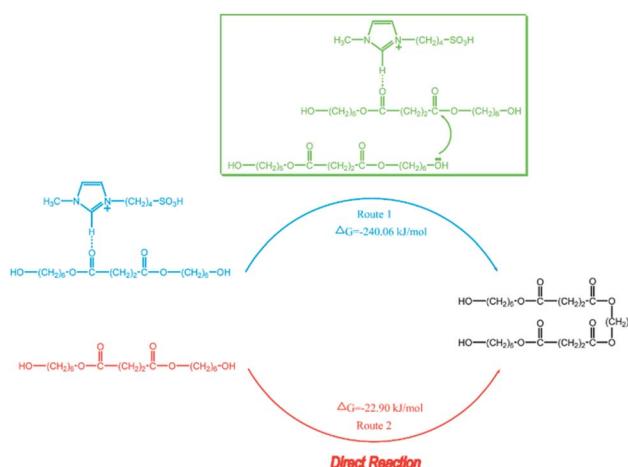
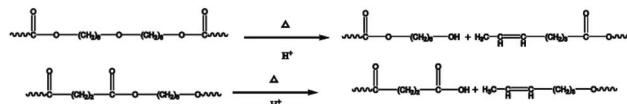


Fig. 8 The DFT calculations of free energies of esterification process with or without cation of SFBAILs catalysis (model based on Tang's work).



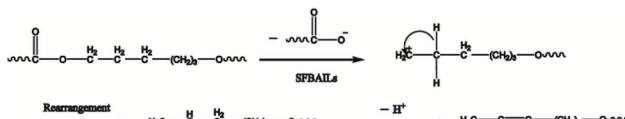


Scheme 4 Formation of double bonds through esters or ethers.

sulfonate esters means less side reactions. When compared the free energy of corresponding reactions in $[\text{BSMIM}][\text{TFS}]$ and $[\text{BBSIm}][\text{HSO}_4]$ at 373.15 K, as shown in Fig. 6, the free energy of esterification in our case is $71.18 \text{ kJ mol}^{-1}$ and $167.70 \text{ kJ mol}^{-1}$ in Fradet's case. The difference of ΔG between two esterification reactions implies that the main reaction between 1,6-hexanediols and succinic acid is easier to happen than dodecan-1-ol and dodecanoic acid. Hence, since the main reaction route in our case is easier to happen, and less sulfonate esters will be formed, and ethers formation in $[\text{BSMIM}][\text{TFS}]$ and $[\text{BSMIM}][\text{HSO}_4]$ is more possible to happen. However, this seems not explain why ethers found only in $[\text{BSMIM}][\text{TFS}]$, and maybe this cause by the stronger acidity and more sulfonic acid in $[\text{BSMIM}][\text{TFS}]$, which promotes the etherification process.

In addition, the resonance at 5.35 ppm reflects the formation of double bonds (Schemes 4 and 5). In this case, the double bonds may be caused by the dehydration of the $-\text{OH}$ end-group catalyzed by SFBAILS or the scission of ester bonds and ether bonds, which is similar to other polyesters in SFBAILS.²⁵

Possible mechanism of post-polycondensation in SFBAILS. The mechanism of post-polycondensation in SFBAILS was investigated with the DFT method. In Tang's recent work,²⁶ the polycondensation of poly(ethylene 2,5-furandicarboxylate) in $[\text{C}_2\text{MIM}]\text{BF}_4$ was found to go through the formation of hydrogen bond between ionic liquids and carbonyl oxygen, which helped the $-\text{OH}$ group to attack carbonyl oxygen. Under such a premise, the model of SFBAILS and reactants was established and the result was listed in Fig. 8. For post-polycondensation of



Scheme 5 The possible mechanism of the formation of double bonds through esters or ethers.

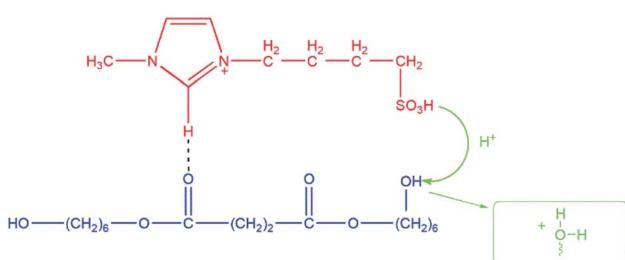


Fig. 9 The optimization model of hydrogen bonds between intermediate and cation of SFBAILS catalysis.

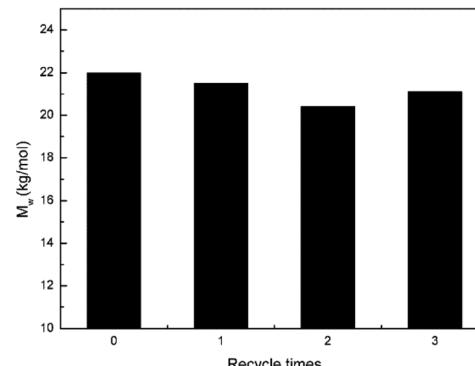


Fig. 10 Post-polycondensation of 1,6-hexanediol and succinic acid after 3 recycled times.

poly(hexylene succinate) in SFBAILS, DFT calculations show that when the reaction went through the formation of hydrogen bond process (route 1), the free energy is about 217 kJ mol^{-1} less than the free energy of the reaction without bond formation at 110°C (route 2). This result shows that the cations of SFBAILS catalyzed the post-polycondensation stage by the hydrogen bond between carbonyl oxygen and the hydrogen on imidazole ring, moreover, the optimization result shows that the sulfonic acid group on cations of SFBAILS can play as a proton donor and $-\text{OH}$ group is the acceptor, and this can also promote the esterification process (Fig. 9).

Recycle of SFBAILS

As "green" solvents, SFBAILS have good recyclability. SFBAILS can be easily recycled by using deionized water or isopropanol. The results of post-polycondensation in $[\text{BSMIM}][\text{HSO}_4]$ after being recycled thrice are showed in Fig. 10. There is no big difference in molecular weights, showing that $[\text{BSMIM}][\text{HSO}_4]$ has good recyclability in this reaction system.

Conclusions

In conclusion, the polycondensation process and post-polycondensation process of the biomass material of poly(hexylene succinate) in SFBAILS have been investigated. The polycondensation process in 9 h fits well with the third-order reaction model and there is no obvious viscosity limitation. The post-polycondensation process in SFBAILS was influenced by the temperature, the acidity and thermostability of SFBAILS, and the water removal method. In this system, the type of cations or anions of SFBAILS has no evident effect on the molecular weight. The kinetic study indicates that the post-polycondensation process is a SFBAILS acid-catalyzed polymerization, and can be evaluated by the second-order reaction model. After 30 min of polymerization, the system becomes inevitably viscous and limits the growth of molecular weight of poly(hexylene succinate). In addition, the formation of ethers was found in poly(hexylene succinate) in $[\text{BSMIM}][\text{TFS}]$, and double bonds was found in both SFBAILS. The anions of SFBAILS may play an important role in the formation of ethers



during the post-polycondensation process. As DFT results show, during the post-polycondensation stage, both the imidazole ring and the sulfonic group on cations of SFBAILS participate in the catalytic process. Finally, the recycled SFBAILS keep their excellent performance after 3 recycles, and this is a completely green polymerization reaction.

Experimental

Materials

N-Methylimidazole (99%), pyridine (99.8%), 1,4-butyl sultone (99%), tetrafluoroboric acid (50% aqueous solution), methanesulfonic acid (99.5%), trifluoromethanesulfonic acid (98%), and 2,4-dichloro-6-nitroaniline (98%) were purchased from Aladdin (Shanghai, China). Sulfuric acid (98%), and *p*-toluene sulfonic acid monohydrate (98%) were purchased from Beijing Chemical Works (Beijing, China). All solvents were purchased from Beijing Tong Guang Fine Chemicals Company. All chemicals were used as received.

Characterization

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at room temperature and the CDCl_3 solution containing 0.03% of tetramethylsilane (TMS) was used as an internal standard. Thermogravimetric analysis (TGA) was performed with a METTLER STRAE SW 9.30 thermogravimetric analyser using nitrogen flow as protective gas, and the heating rate is 10 K min^{-1} . The UV spectra were recorded on a PGGeneral TU-1901 UV-vis spectrophotometer at 50°C , and 2,4-dichloro-6-nitroaniline was used as an indicator at the concentration of 25 mg L^{-1} in SFBAILS. The calibration curve was made by using the unprotonated indicator which was dissolved in chloroform at concentrations of $5\text{--}25 \text{ mg L}^{-1}$, and the correlation coefficient is 0.9954.

Synthesis of SFBAILS

All SFBAILS were synthesized as previously described.²⁷ The mole ratio of *N*-methylimidazole or pyridine with sulfuric acid (98%) is 1 : 1 to obtain the zwitterions at 80°C in toluene. Zwitterions were washed by ethyl acetate and dried under vacuum at 60°C overnight. Then zwitterions were mixed with equimolar protonic acids to obtain the corresponding SFBAILS. SFBAILS were washed with ethyl acetate 5 times and dried in vacuum at 80°C for 48 h.

Synthesis of oligo(hexylene succinate)

The general procedure is as follows²⁸: 29.523 g (0.25 mol) of succinic acid was mixed with slightly excessive 1,6-hexanediol of 30.488 g (0.258 mol) in a glass tube equipped with a nitrogen inlet, a nitrogen outlet and a magnetic stirrer. The mixture was heated at 160°C for 1–12 h. After cooling to room temperature, white and crisp solids were obtained. The product was confirmed by ^1H NMR.

Post-polycondensation of oligo(hexylene succinate) in SFBAILS

A typical method as follows: the post-polycondensation procedure is as follows: 0.4484 g oligo(hexylene succinate) and 0.3164 g (1 mmol) [BSMIM][HSO₄] were introduced in a glass tube with a nitrogen inlet, a nitrogen outlet and a mechanical stirrer. Then, the glass tube was placed in an oil bath at 110°C under nitrogen flow (500 mL min⁻¹). At the end of the reaction, 10 mL of isopropanol was added and the mixture was heated under reflux for 10 min to eliminate the remaining ionic liquid. After cooling, the precipitate was filtrated and washed with 10 mL of isopropanol and 5 mL of diethyl ether. Then the product was dried in vacuum at 45°C overnight. The final product was examined by ^1H NMR spectra and no impurity were detected except the double bonds and ethers caused by the side reactions.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 C. B. Field, M. J. Behrenfeld, J. T. Randerson and P. Falkowski, *Science*, 1998, **281**, 237–240.
- 2 S. Lems, H. J. van der Kooi and J. de Swaan Arons, *Green Chem.*, 2002, **4**, 308–313.
- 3 J. Deng, M. Li and Y. Wang, *Green Chem.*, 2016, **18**, 4824–4854.
- 4 C. Vilela, A. F. Sousa, A. C. Fonseca, A. C. Serra, J. F. J. Coelho, C. S. R. Freire and A. J. D. Silvestre, *Polym. Chem.*, 2014, **5**, 3119–3141.
- 5 A. Kaoukabi, F. Guillen, H. Qayouh, A. Bouyahya, S. Balieu, L. Belachemi, G. Gouhier and M. Lahcini, *Ind. Crops Prod.*, 2015, **72**, 16–23.
- 6 G.-X. Chen, H.-S. Kim, E.-S. Kim and J.-S. Yoon, *Eur. Polym. J.*, 2006, **42**, 468–472.
- 7 A. Fradet and M. Tessier, in *Synthetic methods in step-growth polymers*, ed. M. E. Rogers and T. E. Long, J. Wiley & Sons, New York, 2003, ch. 2, pp. 17–132.
- 8 T. Erdmenger, C. Guerrero-Sanchez, J. Vitz, R. Hoogenboom and U. S. Schubert, *Chem. Soc. Rev.*, 2010, **39**, 3317–3333.
- 9 S. Dewilde, W. Dehaen and K. Binnemans, *Green Chem.*, 2016, **18**, 1639–1652.
- 10 J. Wang and Z. Liu, *Green Chem.*, 2012, **14**, 3204–3210.
- 11 J. Dou and Z. Liu, *Green Chem.*, 2012, **14**, 2305–2313.
- 12 (a) A. Basterretxea, E. Gabirondo, A. Sanchez-Sanchez, A. Etxeberria, O. Coulembier, D. Mecerreyres and H. Sardon, *Eur. Polym. J.*, 2017, **95**, 650–659; (b) A. Sanchez-Sanchez, A. Basterretxea, D. Mantione, A. Etxeberria, C. Elizetxea, A. de la Calle, S. García-Arrieta, H. Sardon and D. Mecerreyres, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 2394–2402.
- 13 A. S. Amarasekara and N. C. Okorie, *Catal. Commun.*, 2018, **108**, 108–112.



14 Z. Xue, L. Qin, J. Jiang, T. Mu and G. Gao, *Phys. Chem. Chem. Phys.*, 2018, **20**, 8382–8402.

15 (a) E.-M. Dukuzeyezu, H. Lefebvre, M. Tessier and A. Fradet, *Polymer*, 2010, **51**, 1218–1221; (b) S. Zhang, V. Lemaire, A. Féret, H. Lefebvre, M. Tessier and A. Fradet, *Polym. Chem.*, 2013, **4**, 1538–1545.

16 Q. Peng, K. Mahmood, Y. Wu, L. Wang, Y. Liang, J. Shen and Z. Liu, *Green Chem.*, 2014, **16**, 2234–2241.

17 C. Gao, X. Zhang, J. Sun, Z. Yuan, S. Han, Y. Liu and S. Ji, *J. Appl. Polym. Sci.*, 2018, **135**, 46388.

18 H. Xing, T. Wang, Z. Zhou and Y. Dai, *J. Mol. Catal. A: Chem.*, 2007, **264**, 53–59.

19 (a) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, 1932, **54**, 2721–2739; (b) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, 1963, **85**, 878–883.

20 D. He, Y. Wu, Z. Liu and T. Zhao, *RSC Adv.*, 2017, **7**, 39604–39610.

21 G. Odian, *Principles of polymerization*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2004.

22 S. Zhang, A. Feret, H. Lefebvre, M. Tessier and A. Fradet, *Chem. Commun.*, 2011, **47**, 11092–11094.

23 S. Zhang, H. Lefebvre, M. Tessier and A. Fradet, *Green Chem.*, 2011, **13**, 2786–2793.

24 Y. Jing, R. Zhu, C. Liu and D. Zhang, *J. Org. Chem.*, 2017, **82**, 12267–12275.

25 T. J. Schildhauer, I. Hoek, F. Kapteijn and J. A. Moulijn, *Appl. Catal., A*, 2009, **358**, 141–145.

26 X. L. Qu, M. Jiang, B. Wang, J. Deng, R. Wang, Q. Zhang, G. Y. Zhou and J. Tang, *ChemSusChem*, 2019, **12**, 4927–4935.

27 (a) A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, *J. Am. Chem. Soc.*, 2002, **124**, 5962–5963; (b) M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057–1062.

28 C. Fu and Z. Liu, *Polymer*, 2008, **49**, 461–466.

