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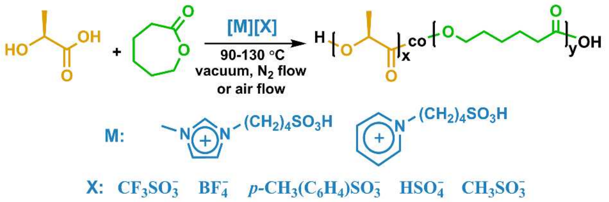

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Qiaohong Peng, Khalid Mahmood, Ying Wu, Leli Wang, Yanyan Liang, Jianan Shen and Zhengping Liu*

Biodegradable copolymers of L-lactic acid and ε-caprolactone [P(LLA-CL)s] were prepared in sulfonic acid-functionalized Brønsted acidic ionic liquids (SFBAILs) with very different anions and cations. SFBAILs work as both solvents and catalysts. The copolymerization process was proved to be a combination of polycondensation and simultaneous transesterification after a fast ring-opening polymerization of ε-caprolactone through kinetic study. Copolymers with different monomer ratios were obtained. We found that the anions rather than the cations of SFBAILs have a great impact on the polymerizations. In addition, SFBAILs can be simply recovered by phase separation and recycled without decreasing efficiency.

Introduction

Both poly(lactic acid) and poly(ε-caprolactone), biodegradable and biocompatible polymers, have been widely investigated and applied.[1] Generally, their synthesis was through polycondensation and/or ring-opening polymerization. It is suitable to produce poly(ε-caprolactone) by ring-opening polymerization because ε-caprolactone is more available and stable than 6-hydroxyhexanoic acid. But it is more facile to produce poly(lactic acid) by polycondensation of lactic acid rather than ring-opening polymerization of lactide which is derived from the former via several complicated processes. Moreover, in ring-opening polymerization, rigorous conditions (e.g., high purity of monomers, inert atmosphere) are necessary in order to achieve high molecular weight polymers and it is inevitable to use transition metal catalysts that are difficult to be separated from polymers. Combination of polycondensation and ring-opening polymerization of linear monomer, lactic acid and ring monomer, ε-caprolactone was little investigated, especially in ILs, presumably because of its complexity.[2]

Ionic liquids, employed as a novel and environmentally benign solvents, instead of classical organic ones, have shown great improvements in chemical process, for example, organic synthesis and polymer preparation.[3] Due to their distinctive physicochemical properties of low volatility, high ionic conductivity, wide electrochemical window, thermal and chemical stability, ability to dissolve organic/inorganic solutes and gases, and tunability of cations and anions, ionic liquids have been attracting great attentions in many fields.

Polycondensation generally needs harsh conditions (e.g. high temperature, high vacuum, etc.) in order to remove condensed small molecules from viscous reaction system and to achieve high conversions and high molecular weights. It seems to be reasonable to take ionic liquids as reaction media in polycondensation since ionic liquids as "green solvents" are of negligible volatility, chemical stability, thermostability, etc.[4]

Polycondensation in ionic liquids has been well investigated in the past decade.[5] Medium and high molecular weight polyimides, polyamides,[6] polyesters,[7] phenol-formaldehyde resins,[8] polysulfones,[9] poly(aryl ether ketone)s[10] and poly(ether ether ketone)s,[11] have been synthesized through polycondensation in conventional ILs by our and other research groups.

In recent years, there has been a growing interest in Brønsted acidic ionic liquids (BAILs), a class of task-specific ionic liquids. They are stable to water and air as compared with Lewis acidic ionic liquids such as chloroaluminate ionic liquids. Condensation reactions of small molecules in BAILs have been extensively reported but there are only a few studies addressing condensation polymerizations in BAILs.

BAILs supplied a very efficient way to synthesize ethyl acetate, and the products can be isolated and recycled in a very simple route at the end of reaction.[12] Bazureau *et al.* compared several imidazolium BAILs bearing different anions, and found that anions have a distinct effect on the rate of esterification.[13] Wang *et al.* reported esterification of benzoic acid with simple alcohols in sulfonic acid-functionalized pyridinium ionic liquids.[14] The most immiscible ionic liquids with the products led to the greatest shift of the esterification reaction equilibrium to the product side. Hammett acidity measurements revealed different reaction rate resulted from different acidities of ionic liquids.

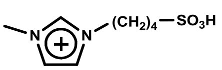
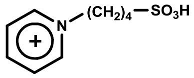
Fradet's research group has done some work related to polycondensation in BAILs. They synthesized high molar mass polyesters of 12-hydroxydodecanoic acid in HSO_4-anionic BAILs at low temperature, in short reaction time, and without any added catalyst under nitrogen flow.[15] Later on, high molar mass linear polyethers were synthesized by simple direct polyetherification of diols with 7 to 12 methylene units in Tf_2N-anionic BAILs at relatively low temperatures.[16] Most recently, Linear polyesters of diols and diacids and hyperbranched polyesters of 2,2-bis(hydroxymethyl)propanoic acid were successfully obtained via polycondensation in 3-butyl-1-(butyl-4'-sulfonic acid)imidazolium hydrogen sulfate ([BBSIM][HSO_4]). These all demonstrate the advantages of BAILs as solvents and catalysts.

In this report, we investigate a particular and complicated copolymerization of a linear monomer L-lactic acid and a ring monomer ε-caprolactone, including polycondensation and ring-opening polymerization mechanisms, especially in sulfonic acid-functionalized Brønsted acidic ionic liquids (SFBAILs). Even more than that, the actual polymerization process was proposed by tracing the structural changing of copolymers using NMR spectroscopy. This is a facile route to realize copolymerization of L-lactic acid and ε-caprolactone since ionic liquids applied here work as both solvents and catalysts and the final products can be simply separated from ionic liquids. In addition, the acidity and thermostability of SFBAILs and miscellaneous copolymerization conditions as well as their influence on copolymerizations were investigated and discussed in detail.

Results and discussion

In this study, six sulfonic acid-functionalized Brønsted acidic ionic liquids (SFBAILs) were synthesized and employed as solvents as well as catalysts to investigate the copolymerization of L-lactic acid (LLA) and ε-caprolactone (CL). These SFBAILs bear different anions and cations as shown in Table 1. As known to all, esterification can be efficiently catalyzed by many Brønsted acids, such as the best-known H_2SO_4, *p*-toluene sulfonic acid, etc. But these well-known acids are of either instability or volatility or even solidity, which are not appropriate as solvents. SFBAILs open a new door to improve chemical process as solvents and catalysts.

Table 1 Structures and Hammett acidities (H_0) of sulfonic acid-functionalized Brønsted acidic ionic liquids

SFBAILs	Cations	Anions	H_0^a
[BSMIM][TFS]		$CF_3SO_3^-$	-4.1
[BSMIM][BF$_4$]		BF_4^-	-3.7
[BSMIM][TS]		*p*-$CH_3(C_6H_4)SO_3^-$	-3.5
[BSMIM][HSO$_4$]		HSO_4^-	-3.3
[BSMIM][MS]		$CH_3SO_3^-$	-3.3
[BSPy][HSO$_4$]		HSO_4^-	-3.3[b]

[a] The Hammett acidities of SFBAILs were determined using the Hammett method with UV-Vis spectroscopy at 50 ℃, 25 mg/L of 2,4-dicholoro-6-nitroaniline were used as indicator. [b] From reference 32.

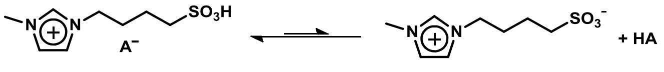
Acidity of protonic acids and corresponding SFBAILs

Herein, the acidity of SFBAILs was evaluated by Hammett acidity functions (H_0), using UV-vis spectroscopy. The Hammett method is effectively and widely applied to evaluate the protonation extent of uncharged indicator bases in solution, in terms of the measurable ratio [I]/[IH$^+$]. The Hammett acidity function is defined as:[17]

$$\boldsymbol{H_0 = \mathrm{p}K(\mathrm{I})_{aq} + \log([\mathrm{I}]/[\mathrm{IH}^+])}$$

where p$K(\mathrm{I})_{aq}$ is the pK_a value of the indicator referred to an aqueous solution, [IH$^+$] and [I] are the molar concentrations of protonated and unprotonated form of the indicator in SFBAILs, respectively. The p$K(\mathrm{I})_{aq}$ of indicator 2,4-dichloro-6-nitroaniline used here is -3.31. [I]/[IH$^+$] ratio was determined by UV-vis spectroscopy.[14b] The results were summarized in Supporting Information (Figure S1, Figure S2 and Table S1).

Protonic acids which were used to synthesize SFBAILs are all strong acids but possess significantly different acidities with Hammett acidities H_0 in the range of -7 to -14.[18] Moreover, H_0 values of organic sulfonic acids range from -5.8 to -7.9,[19] which were considered to be in acidity range of SFBAILs. However, as shown in Table 1, determined H_0 values of SFBAILs are in the range of -3.3 to -4.1, which are similar to that of pyridinium-type sulfonic acidic ionic liquids according to the literature.[14b] Decrease of acidity as compared with conventional organic sulfonic acids is probably attributed to combination of concentrated anions of SFBAILs with protons, which makes the dissociation more difficult (Scheme 1). Among the SFBAILs, anions seem not to exhibit great influence on acidity of SFBAILs because of their same sulfonic acid group which deserves the acid strength.



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

Thermostability of SFBAILs

Thermostability of SFBAILs as solvents in polycondensation is very important because polycondensation usually needs relatively high reaction temperature. Most of ionic liquids possess excellent thermostability, whereas introducing sulfonic groups to ionic liquids presents different results. Figure 1 shows the thermogravimetric analysis (TGA) of different SFBAILs. The onset decomposition temperatures of these SFBAILs are 357.1 ℃ for [BSMIM][TFS], 323.1 ℃ for [BSMIM][HSO_4], 320.5 ℃ for [BSMIM][TS], 328.9 ℃ for [BSMIM][MS] and 107.7, 319.4 ℃ for [BSMIM][BF_4] corresponding to two decomposition stages. Consequently, [BSMIM][TFS] is the most stable as compared to others. For [BSMIM][BF_4], the weight loss before the second decomposition stage is about 23.5%, which could be ascribed to the loss of BF_3 (22.2 wt%) originating from conversion of [BSMIM][BF_4] to [BSMIM][F]. This can be used to explain why only low molecular weight copolymers were obtained in [BSMIM][BF_4] (Table 2).

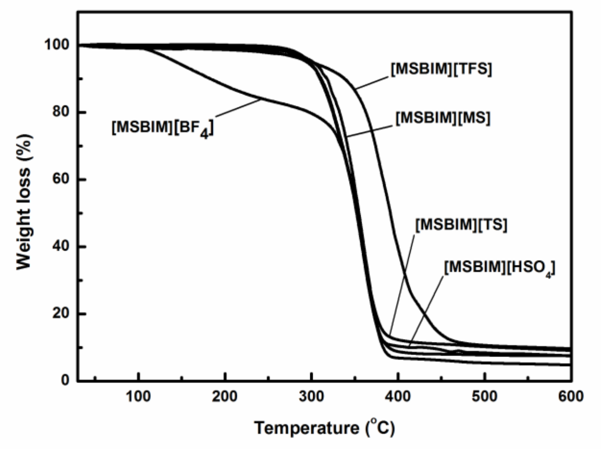


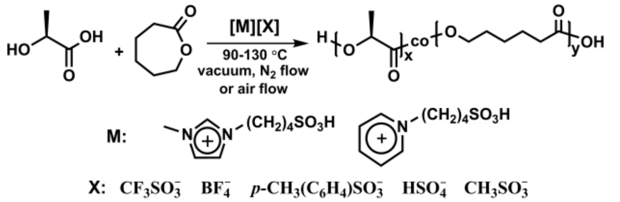
Fig. 1 Thermogravimetric curves of different sulfonic acid-functionalized Brønsted acidic ionic liquids.

Copolymerization of L-lactic acid and ε-caprolactone

SFBAILs used here have different cations and anions. All of cations contain n-butylene sulfonic acid group which is expected to catalyze the polyesterification. These SFBAILs as solvents have good liquidity at reaction temperature although they are viscous liquids or low-melting-point solids (e.g., [BSMIM][TFS]) at room temperature. At the beginning of reactions, L-lactic acid and ε-caprolactone could dissolve in SFBAILs to give a homogenous phase. But the reaction system became heterogenous as polymerization progressed, which is believed to be one of the main reasons that limits increasing of molecular weight.

Miscellaneous polymerization conditions in SFBAILs were investigated in this work (Table 2). It is apparent from Table 2 that, types of SFBAILs, particularly anions, have a great impact on the polymerizations. The weight-average molecular weights of copolymers prepared in [BSMIM][HSO_4] and [BSPy][HSO_4] (same anion but different cations) can achieve 35.6 and 35.9 kDa, respectively, with only a little difference. While the molecular weights varied a lot in imidazolium-type SFBAILs with different anions, especially in [BSMIM][BF_4], due to its instability determined from thermogravimetric analysis as mentioned above (Figure 1). Besides, the molecular weights are not proportional to the acidity of SFBAILs. Copolymerizations of LLA and CL in [BSMIM][TFS], [BSMIM][TS], [BSMIM][MS] at 130 °C only gained medium molecular weight copolymers. Higher temperature was benefit to [BSMIM][TS] and [BSMIM][MS] systems, nevertheless, the molecular weights of copolymers were lowered than 10 kDa when the polymerization temperature decreased to 110 °C. Furthermore, the highest molecular weight copolymer was obtained in [BSMIM][TFS] at 110 °C and the molecular weight could achieved 19.2 kDa even at 90 °C. This is attributed to a trace of trifluoromethanesulfonic acid produced from the dissociation equilibrium (Scheme 1), which can generate more side reactions at elevated temperature. In terms of [BSMIM][HSO_4], the molecular weights could achieved over 30 kDa at both 110 °C and 130 °C due to double catalytic protons included in both cation and anion. Moreover, vacuum, blowing nitrogen and blowing dry air are three ways to remove water produced during the polycondensation reaction. The efficiency of above three ways is in the order of vacuum > blowing nitrogen > blowing dry air. It is worth noting that polymerization can go on successfully even under air, and yielded copolymers have almost the same structure as determined by ^1H NMR (Figure S3) compared with that prepared under vacuum or blowing nitrogen.

Table 2 Copolymerization of LLA and CL in sulfonic acid-functionalized Brønsted acidic ionic liquids[a]



Run	SFBAILs	Temp. (°C)	Water removal[b]	M_w (kDa)[c]	PDI[c]	Yield (%)[d]
1	[BSMIM][TFS]	130	50 Pa	24.9	1.94	81.6
2	[BSMIM][BF_4]	130	50 Pa	2.6	2.34	55.9
3	[BSMIM][TS]	130	50 Pa	26.3	1.80	86.7
4	[BSMIM][HSO_4]	130	50 Pa	35.6	1.68	85.5
5	[BSMIM][MS]	130	50 Pa	22.6	1.90	70.8
6	[BSPy][HSO_4]	130	50 Pa	35.9	1.96	84.0
7	[BSMIM][TFS]	110	50 Pa	38.9	1.84	87.3
8	[BSMIM][TFS]	90	50 Pa	19.2	1.84	90.2
9	[BSMIM][TFS]	110	N_2-flow	31.5	1.80	85.4
10	[BSMIM][TFS]	110	dry air-flow	28.4	1.75	81.5

[a] Polymerization conditions: equimolar of LLA and CL, 50 wt% SFBAIL, polymerization at given temperature for 6 h. [b] In the vacuum system, the reaction pressure gradually decreased from 2 kPa to 50 Pa in 1 h; In the air and nitrogen flow systems, flow rate of 200 mL/min applied over the reaction. [c] Determined by GPC calibrated with polystyrene standard. [d] The yields were calculated without precipitation of polymers.

The molecular weights of P(LLA-CL) copolymers are plotted in Figure 2 as function of weight percentage of [BSMIM][TFS]. As indicated in Figure 2, molecular weights of copolymers were significantly influenced by the concentration of SFBAILs. The polymerization efficiency was drastically lowered in both concentrated and dilute polymer solutions in SFBAILs, but medium concentrations, e.g., 30 % and 50 %, are benefit to polymerization. That's because it is difficult to remove water in concentrated solution and reaction probability of functional groups was reduced in dilute solution.

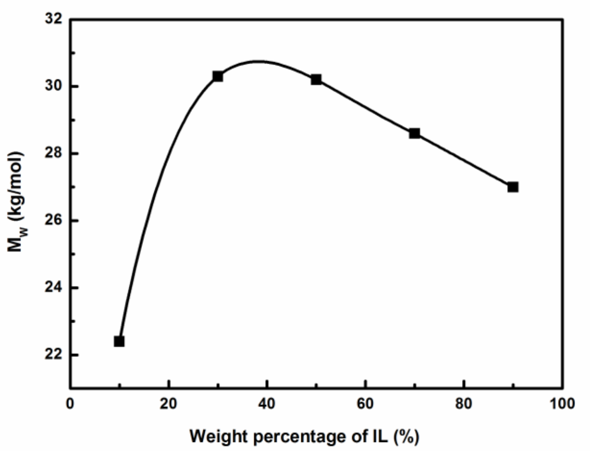


Fig. 2 The relationship between M_w of P(LLA-CL) and weight percentage of [BSMIM][TFS] (110 °C, 50 Pa, 6h).

The molecular weights of copolymers with different reaction time were measured and the results were shown in Figure 3. Figure 3 indicates the molecular weights of copolymers increase with the reaction time in 9 h. But after polymerization for 3 h, growth rate of polymers slows down and no obvious increase of molecular weights is observed. This is because viscous polymer solution limits the movement of polymer chains, and continues to decrease the probability of reaction. Such phenomenon exists in plenty of polymerizations. In addition, a weight-average molecular weight of about 47 kDa can be achieved in [BSMIM][TFS] after 20 h.

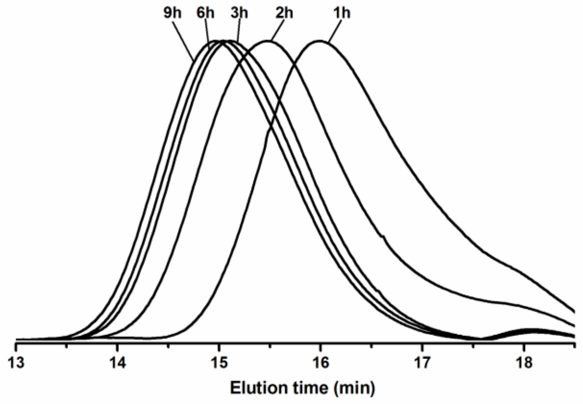


Fig. 3 Variation of SEC chromatograms of P(LLA-CL)s with reaction time (in [BSMIM][TFS], 110 °C).

Copolymers with different monomer compositions are also synthesized in SFBAILs, and Figure 4 illustrates that compositions of copolymers agree well with initial monomer ratios. It supplies an effective way to tune the structures and properties of copolymers. Homopolymerizations of LLA and CL were also investigated and only low molecular weight polymers were obtained in both cases. In respect of LLA, its polymer, poly(L-lactic acid), has high melting point about 170 ℃ and its poor solubility in SFBAILs causes it to precipitate out from SFBAILs at the beginning of polymerization. Similarly, poly(ε-caprolactone) is also immiscible with SFBAILs and forms two layers after stopping stirring.

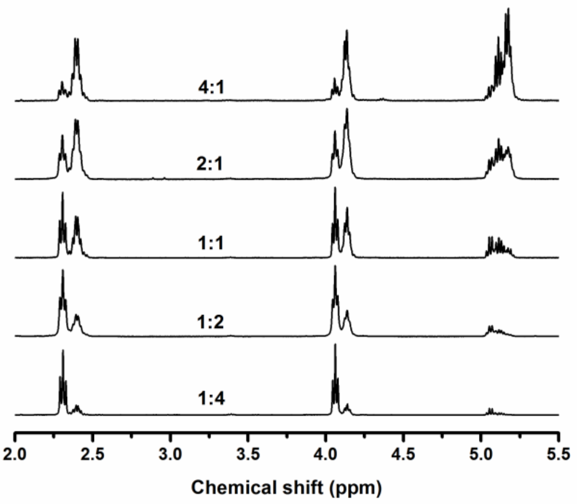


Fig. 4 ^{1}H NMR spectra of P(LLA-CL) prepared in [BSMIM][TFS] with different initial molar ratio of LLA to CL.

Copolymerization mechanism and kinetic study

The copolymerization process was monitored at intervals of 20 and 40 minutes by ^{1}H NMR in $CDCl_3$. SFBAILs' signals could not be detected due to immiscibility of SFBAILs in $CDCl_3$. Figure 5 shows ^{1}H NMR spectrum of copolymer of LLA and CL in [SBMIM][TFS]. Almost all of CL monomers converted into polymers (2.2-2.5 ppm and 4.0-4.2 ppm) from ring structure (2.6 ppm and 4.2 ppm) in just 20 minutes and the main bonding way was caprolactate to caprolactate (**CC**, 2.3 ppm and 4.05 ppm) rather than lactate to caprolactate (**LC**, 2.4 ppm and 4.15 ppm). Hydroxyl end group of caprolactate and lactate were located at 3.66 ppm and 4.36 ppm, respectively. Resonance at 4.27 ppm was assigned to methine of LLA. Accordingly, at this reaction stage, ring-opening of CL was the primary polymerization mode, followed by condensation polymerization accompanied with transesterification (Scheme 2). Increasing randomness of copolymer, as shown in Figure 6, and propagation of polymer chain confirmed this hypothesis. Degree of randomness was calculated by the following formula:

$$\text{Degree of randomness} = \frac{N(\mathbf{LC}) + N(\mathbf{CL})}{N(\mathbf{LL}) + N(\mathbf{CC})} = \frac{N(\mathbf{LC})}{N(\mathbf{CC})}$$

Where N(**LC**), N(**CL**), N(**LL**) and N(**CC**) stand for the number of different bonding ways between lactate and caprolactate in

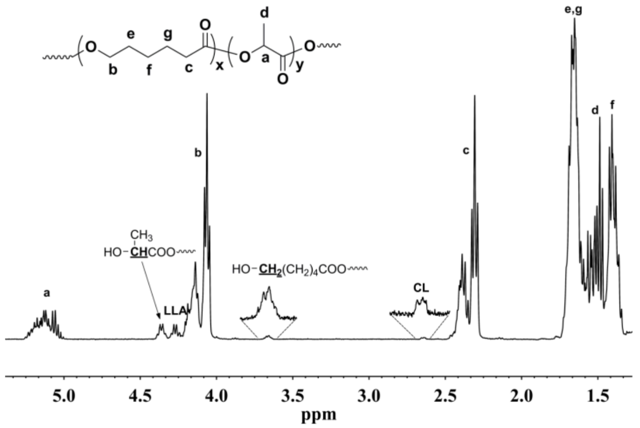


Fig. 5 ^{1}H NMR spectrum of P(LLA-CL) copolymers synthesized in [SBMIM][TFS] at 20th minute ($CDCl_3$, 400 MHz).

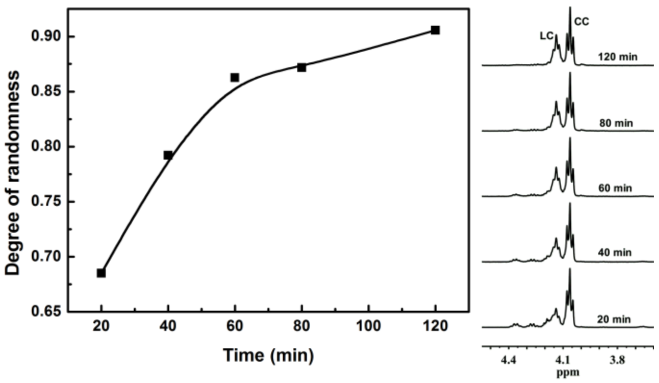
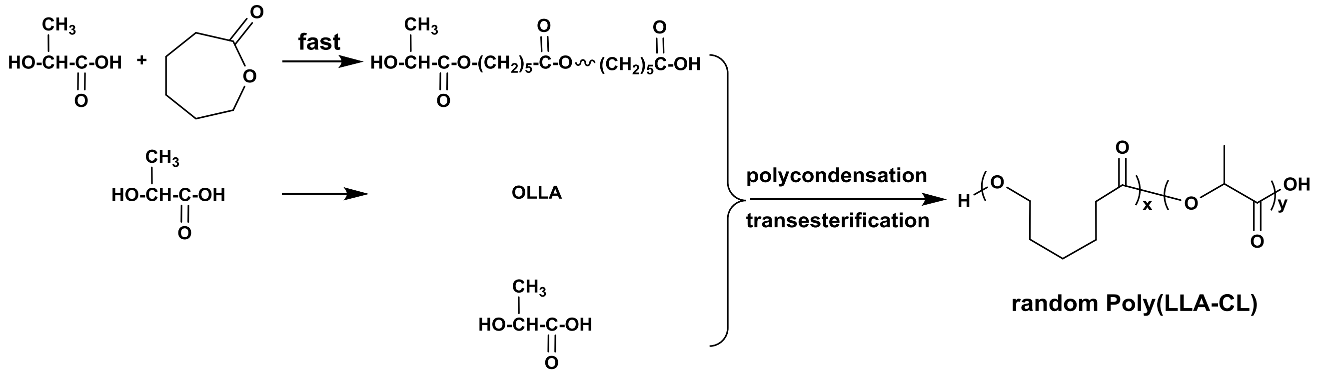


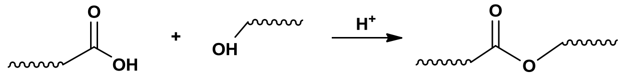
Fig. 6 Degree of randomness of copolymers as function of reaction time based on ^{1}H NMR (L and C representing lactate and caprolactate in copolymer chain, respectively).



Scheme 2 Copolymerization process of LLA and CL in SFBAILs.

copolymer chains. N(**LC**) must be equal to N(**CL**) due to the mutual authentication between lactate and caprolactate. And N(**LL**) is also equal to N(**CC**) by deducting the same amount of lactate units and caprolactate units in **L-C** bonds. As polymerization progressed, the degree of randomness approached to 1 based on the ^{1}H NMR spectrum of final copolymers (Figure S4). The constant degree of randomness of copolymers demonstrates that caprolactate and lactate have nearly the same transesterification reactivity upon the polycondensation stage.

Polycondensation following fast ring-opening polymerization can be considered as an acid-catalyzed second-order reaction. A simplified reaction equation was given as follows:



So second-order rate equation can be defined as:

$$\frac{1}{[\mathrm{OH}]} = \mathrm{kt} + \mathrm{Con.} \quad \mathrm{OR} \quad \frac{1}{[\mathrm{COOH}]} = \mathrm{kt} + \mathrm{Con.}$$

Concentration of reactive functional group -OH (or -COOH) can be figured out from ^{1}H NMR spectra according to different chemical shifts between polymer chain and end group. In Figure 7, the concentration of -OH (or -COOH) was defined as mole numbers per kilogram polymers. In addition, we can know from Figure 7 that the polymerization rate constant in [BSMIM][TFS] and [BSMIM][HSO_4] were 14.6×10^{-3} kg mol^{-1} min^{-1} and 6.70×10^{-3} kg mol^{-1} min^{-1}, respectively, as compared with the rate constant (13×10^{-3} kg mol^{-1} min^{-1} at 109 ℃) of

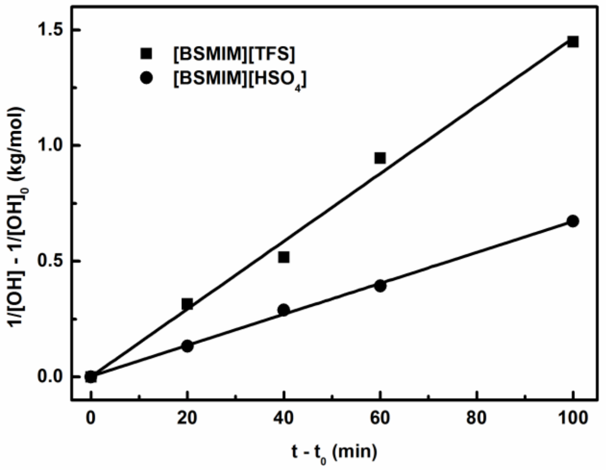


Fig. 7 Variation of (1/[OH] – 1/$[OH]_0$) versus reaction time (t - t_0) of copolymerization of LLA and CL in [BSMIM][TFS] and [BSMIM][HSO_4] at 110 °C.

p-toluenesulfonic acid-catalyzed polyesterification of diacid and diol.[20] The former is about twice as fast as the latter, which is consistent with the already determined Hammett acidities. The polymerization rate is proportional to acid strength.

Recycle of SFBAILs

Ionic liquids were referred as "green" solvents not only because of its non-volatility and stability but also the recyclability. SFBAILs can be recycled in a very simple way by phase separation, ionic liquids in bottom phase and polymers in upper phase (Figure S5). From Figure 8, one can see that [SBMIM][TFS] have almost the same good performance after four recycles, since no big difference of molecular weights was observed under the identical polymerization conditions. In addition, ^{1}H NMR spectrum of recycled [SBMIM][TFS] have a close match with freshly prepared one (Figure S6). It can be concluded that SFBAILs have excellent recyclability in this copolymerization system.

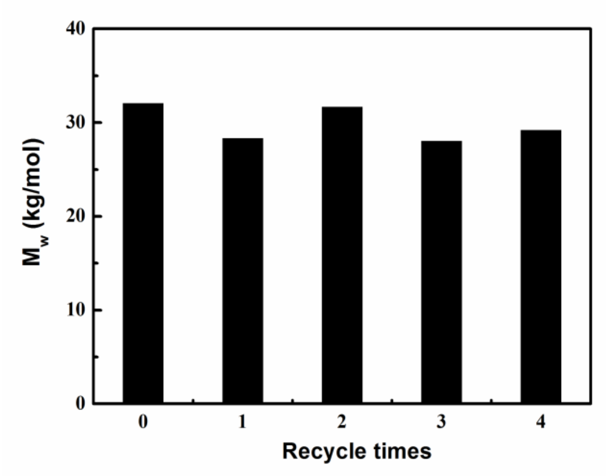


Fig. 8 Copolymerization of L-lactic acid and ε-caprolactone in recycled [SBMIM][TFS].

Conclusions

In this work, copolymerizations of L-lactic acid and ε-caprolactone in sulfonic acid-functionalized Brønsted acidic ionic liquids (SFBAILs) were investigated comprehensively. Determined Hammett acidities show that the acidity of SFBAILs is weaker than conventional organic sulfonic acids, as a result of concentrated anions of ionic liquids. The polymerization process was influenced by temperature, concentration, acidity and thermostability of SFBAILs, method to remove water, etc. Cations of SFBAILs have no obvious effect on the copolymerization, oppositely, anions play an important role in it. Copolymers with different compositions were also achieved by controlling initial monomer ratios. Thus, it supplied a facile way to tune the properties of copolymers. Kinetic study indicates that copolymerization process was combined by polycondensation and simultaneous transesterification after a fast ring-opening polymerization of ε-caprolactone. Moreover, SFBAILs that were conveniently recovered by way of phase separation still possess excellent performance after four recycles.

Experimental

Materials

N-methylimidazole (Linhai Kaile Chemical Factory, China) was dried with calcium hydride under stirring and then distilled under reduced pressure before use. 1,4-butyl sultone (99%), tetrafluoroboric acid (50% aqueous solution), L-lactic acid (99%), ε-caprolactone (99%) were purchased from Aladdin (Shanghai, China). Methanesulfonic acid was purchased from Alfa Aesar (Tianjin, China). 2,4-dichloro-6-nitroaniline (98 %) was purchased from Combi-Blocks Inc. Pyridine (99.5%), Sulfuric acid (98%), p-toluene sulfonic acid monohydrate (98%) and all the solvents were purchased from Beijing Chemical Works (Beijing, China). These chemicals were used as received.

Characterization

NMR spectra were recorded at room temperature on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 solutions containing 0.03% of tetramethylsilane (TMS) as an internal standard. Thermogravimetric analysis (TGA) was performed with a METTLER STRAE SW 9.30 thermogravimetric analyzer under nitrogen flow at a heating rate of 10 ℃/min. The decomposition temperatures were measured at the onset point of the thermogravimetric curve. The molecular weight analysis was performed using a Polymer Laboratories gel permeation chromatograph (PL-GPC 50) equipped with PL gel mixed-B columns and RI detector. Chloroform was used as eluent at a flow rate of 1.0 mL/min at 40 ℃. Polystyrene standards were used to calibrate the system. The UV spectra were recorded on a PGeneral TU-1901 UV-vis spectrophotometer at 50 ℃ using 2,4-dichloro-6-nitroaniline as an indicator with 25 mg/L concentration in SFBAILs. The calibration curve was made using chloroform solutions of the indicator in the unprotonated form with the concentrations from 5 to 25 mg/L. The correlation coefficient is higher than 0.999.

Synthesis of Ionic Liquid

Zwitterion 1-(4'-butane sulfonate)-3-methylimidazolium and ionic liquids 1-(butyl-4'-sulfonic acid)-3-methylimidazolium trifluoromethanesulfonate [BSMIM][TFS], 1-(butyl-4'-sulfonic acid)-3-methylimidazolium hydrosulfate [BSMIM][HSO_4], 1-(butyl-4'-sulfonic acid)-3-methylimidazolium p-toluenesulfonate [BSMIM][TS], 1-(butyl-4'-sulfonic acid)-3-methylimidazolium methanesulfonate [BSMIM][MS], 1-(butyl-4'-sulfonic acid)-3-methylimidazolium fluoborate [BSMIM][BF_4], and 1-(butyl-4'-sulfonic acid)pyridinium hydrosulfate [BSPy][HSO_4] were synthesized as previously described.[12, 21] IL identity and indeed purity were confirmed by ^{1}H NMR, ^{13}C NMR and elemental analysis (Supporting Information).

Copolymerization of L-lactic acid and ε-caprolactone in SFBAILs

The general procedure is given as below: 1-(butyl-4'-sulfonic acid)-3-methylimidazolium trifluoromethanesulfonate (2.04 g, 5.54 mmol) and equimolar mixture of L-lactic acid (0.90 g, 10 mmol) and ε-caprolactone (1.14 g, 10 mmol) were charged into a 10 mL reaction tube connected with vacuum line. The air in the reactor was exchanged with a nitrogen flow. Then the reaction tube was placed in an oil bath at 110 ℃ under mechanical stirring. The pressure was gradually decreased to 50 Pa in 1 h, then keep these conditions for 6 h. After cooling to room temperature, 5 mL fresh chloroform was added into the tube to extract the polymers and repeated this step twice. Light yellow ionic liquid and clear polymer solution of chloroform were obtained. Ionic liquid can be reused after vacuum drying. The polymer solution was washed with deionized water for thrice and then evaporated to remove chloroform with a rotary evaporator. The product was further dried under vacuum to give a paste-like polymer. (A procedure for recycle of ionic liquids: after phase separation, the bottom ionic liquid phase was dissolved in 5 mL freshly distilled water. The aqueous solution of ionic liquid was centrifuged to remove trace amount of immiscible copolymer, and then the water was distilled under high vacuum to achieve pure ionic liquid. Upper polymer phase was washed with water and then dried under vacuum to give a paste-like polymer.)

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Notes and references

Institute of Polymer Chemistry and Physics of College of Chemistry, BNU Lab of Environmentally Friendly and Functional Polymer Materials, Beijing Normal University, Beijing 100875, P R China. Fax: +86-10-58802075; Tel: +86-10-58806896; E-mail: lzp@bnu.edu.cn.

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1. (a) A. Rafael, L. Loong-Tak, E. M. S. Susan and T. Hideto, *Poly(lactic acid) : synthesis, structures, properties, processing, and applications*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2010; (b) R. M. Rasal, A. V. Janorkar and D. E. Hirt, *Prog. Polym. Sci.*, 2010, **35**, 338-356; (c) M. A. Woodruff and D. W. Hutmacher, *Prog. Polym. Sci.*, 2010, **35**, 1217-1256; (d) X. Wei, C. Gong, M. Gou, S. Fu, Q. Guo, S. Shi, F. Luo, G. Guo, L. Qiu and Z. Qian, *Int. J. Pharm.*, 2009, **381**, 1-18; (e) A. Arbaoui and C. Redshaw, *Polym. Chem.*, 2010, **1**, 801-826; (f) M. Labet and W. Thielemans, *Chem. Soc. Rev.*, 2009, **38**, 3484-3504.
2. H. Fukuzaki, M. Yoshida, M. Asano, M. Kumakura, T. Mashimo, H. Yuasa, K. Imai and Y. Hidetoshi, *Polymer*, 1990, **31**, 2006-2014.
3. (a) P. Kubisa, *Prog. Polym. Sci.*, 2004, **29**, 3-12; (b) P. Kubisa, *Prog. Polym. Sci.*, 2009, **34**, 1333-1347; (c) S. Mallakpour and Z. Rafiee, *Prog. Polym. Sci.*, 2011, **36**, 1754-1765; (d) S. Mallakpour and Z. Rafiee, *J. Polym. Environ.*, 2011, **19**, 447-484; (e) S. Mallakpour and Z. Rafiee, *J. Polym. Environ.*, 2011, **19**, 485-517; (f) T. Welton, *Chem. Rev.*, 1999, **99**, 2071-2083; (g) J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508-3576; (h) T. Erdmenger, C. Guerrero-Sanchez, J. Vitz, R. Hoogenboom and U. S. Schubert, *Chem. Soc. Rev.*, 2010, **39**, 3317-3333; (i) T. Ueki and M. Watanabe, *Macromolecules*, 2008, **41**, 3739-3749; (j) C. Guerrero-Sanchez, M. Lobert, R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.*, 2007, **28**, 456-464; (k) C. Guerrero-Sanchez, R. Hoogenboom and U. S. Schubert, *Chem. Commun.*, 2006, 3797-3799; (l) C. Guerrero-Sanchez, T. Erdmenger, P. Sereda, D. Wouters and U. S. Schubert, *Chemistry-a European Journal*, 2006, **12**, 9036-9045.
4. J. S. Wilkes, *Green Chem.*, 2002, **4**, 73-80.
5. J. Mun and H. Sim, *Handbook of Ionic Liquids: Properties, Applications and Hazards*, Nova Science Publishers, Incorporated, 2012.
6. (a) E. I. Lozinskaya, A. S. Shaplov and Y. S. Vygodskii, *Eur. Polym. J.*, 2004, **40**, 2065-2075; (b) Y. S. Vygodskii, E. L. Lozinskaya and A. S. Shaplov, *Macromol. Rapid Commun.*, 2002, **23**, 676-680.
7. (a) S. Dali, H. Lefebvre, R. El Gharbi and A. Fradet, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 3025-3035; (b) S. Dali, H. Lefebvre, R. El Gharbi and A. Fradet, *E-Polymers*, 2007; (c) C. Fu and Z. Liu, *Polymer*, 2008, **49**, 461-466; (d) J. Dou and Z. Liu, *Green Chem.*, 2012, **14**, 2305-2313; (e) J. Dou, Z. Liu, K. Mahmood and Y. Zhao, *Polym. Int.*, 2012, **61**, 1470-1476.
8. T. Ogoshi, T. Onodera, T. A. Yamagishi and Y. Nakamoto, *Macromolecules*, 2008, **41**, 8533-8536.
9. J. Wang and Z. Liu, *Green Chem.*, 2012, **14**, 3204-3210.
10. J. Wang and Z. P. Liu, *Chin. Sci. Bull.*, 2013, **58**, 1262-1266.
11. H. Q. N. Gunaratne, C. R. Langrick, A. V. Puga, K. R. Seddon and K. Whiston, *Green Chem.*, 2013, **15**, 1166-1172.
12. 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.
13. J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J. P. Bazureau and J. Hamelin, *Catal. Commun.*, 2002, **3**, 185-190.
14. (a) H. B. Xing, T. Wang, Z. H. Zhou and Y. Y. Dai, *Ind. Eng. Chem. Res.*, 2005, **44**, 4147-4150; (b) H. Xing, T. Wang, Z. Zhou and Y. Dai, *J. Mol. Catal. A: Chem.*, 2007, **264**, 53-59.
15. E.-M. Dukuzeyezu, H. Lefebvre, M. Tessier and A. Fradet, *Polymer*, 2010, **51**, 1218-1221.
16. (a) S. Zhang, A. Feret, H. Lefebvre, M. Tessier and A. Fradet, *Chem. Commun.*, 2011, **47**, 11092-11094; (b) S. Zhang, H. Lefebvre, M. Tessier and A. Fradet, *Green Chem.*, 2011, **13**, 2786-2793.
17. (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-&.
18. (a) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1959, 1096-1105; (b) E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, 1966, **88**, 1177-&; (c) D. Farcasiu and D. Hancu, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2161-2165.
19. A. Koebergtelder and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1975, 226-229.
20. P. J. Flory, *J. Am. Chem. Soc.*, 1940, **62**, 2261-2264.
21. M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057-1062.