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PAPER

A simple and efficient synthetic method for poly(ethylene terephthalate): phenylalkyl pyrrolidinium ionic liquid as polycondensation medium†

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A series of phenylalkyl pyrrolidinium ionic liquids (ILs) ([YBPy][X], Y = NO_2, CH_3, F, H; B = benzyl, phenethyl; X = Tf_2N) were synthesized and found to be environmentally benign reaction media for the preparation of poly(ethylene terephthalate) (PET). ILs with specific functional groups had high thermostabilities and showed interesting properties in synthesizing PET at lower temperature (190–240 °C) and pressure (500 Pa) compared to conventional ILs. PET with M_w up to 1.9×10^4 g mol^{-1} was obtained. The ILs can be easily separated and reused after simple purification except for the PF_6^- ILs. This process provides a valuable and environmentally friendly alternative to the currently available method for the preparation of PET in industry.

Introduction

Since the awareness of green chemistry is progressively increasing, ionic liquids (ILs) have gained considerable attention as promising media for green processes due to their distinctive physicochemical properties of low vapor pressure, high ionic conductivity, excellent thermal and chemical stability and strong solubilizing ability, which makes them attractive in several fields, including synthetic chemistry,[1–5] electrochemistry,[6–8] catalysis,[9–14] and polymerization processes.[15–30] Moreover, the physicochemical properties of ILs can be dramatically altered by varying cations and anions. The facile construction of ILs with suitable structures to optimize the reaction conditions for specific applications continues to drive a wide range of fundamental and applied fields in the current research.

Poly(ethylene terephthalate) (PET) has been found a particularly useful material in many commercial fields. All of these opportunities for PET applications are related to its special properties originating from structural characteristics. As an aromatic polyester, the traditional way to synthesize PET is the melt polycondensation of aromatic dicarboxylic acid and diol. Although it provides an important route to PET, the preparation of PET has not been described as a low-energy and green process from the view of increasing environmental awareness. The melt viscosity increases gradually during the polycondensation process and the removal of small molecules such as water and alcohol becomes difficult. Consequently, preparation of PET usually requires high temperature (>250 °C), high vacuum (10–50 Pa) as well as a long reaction time (several hours) to remove the byproducts in the industrial process. Because of the rigorous reaction conditions, reports of PET performed at milder conditions are quite limited. Given both the problems of preparation of PET and underlying approaches to ionic liquid design, it seems to be an opportunity for ILs to be used for preparation of PET under milder conditions.

To date, the possibility of using ionic liquids in polycondensations has been reported for a number of condensation polymers. Polyamides and polyimides with high molecular weights are prepared in different 1,3-dialkylimidazolium ILs reaction media.[31] High molecular weight poly(12-hydroxydodecanoic acid) can be obtained in Brønsted acid ILs (BAILs) by direct polycondensation at low to moderate temperature (90–130 °C), atmospheric pressure and without adding any catalyst.[16,17] The utilization of ILs as new solvents for the synthesis of optically active polyamides has triggered unprecedented possibilities for the advanced polymer materials.[32–34] However, the molecular weights of polyesters obtained from the polycondensation of hydroxy acids in ILs are low due to the precipitation of the products with increasing of the molecular weights.[35] Investigations into lipase-catalyzed transesterification in ILs have also shown that low molecular weight polymers are afforded due to precipitation of the polyesters in ILs.[36–38] High molecular weight aliphatic polyesters are also produced in conventional ILs (diakylimidazolium salts). The miscibility of polyesters/ILs is the main influencing factor in obtaining high molecular weight polymers in the preparation of aliphatic polyesters in ILs.[39]

It is known that PET can only be dissolved in few traditional organic solvents with high boiling points, high thermostabilities, and some functional groups on benzene rings at 80–200 °C, such as $-NO_2$, –O–, –Cl, –OH, $-CH_3$. According to the principle that a substance is more likely to be dissolved in solvents with a similar molecular structure, phenylalkyl pyrrolidinium ILs with specific functional groups were synthesized and used as polycondensation media for the preparation of PET.

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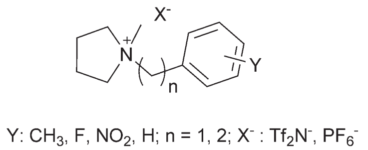
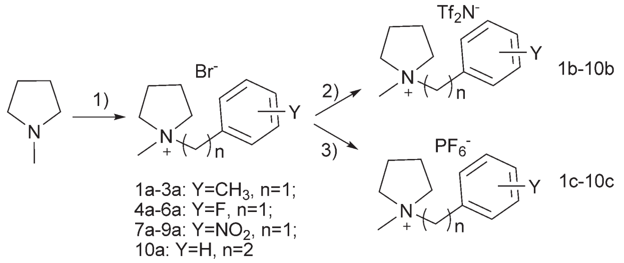


Fig. 1 The structures of phenylalkyl pyrrolidinium ILs.



Scheme 1 Synthesis of phenylalkyl pyrrolidinium ILs. (1) phenylalkyl bromide, N_2, ethyl acetate, stirred, R.T., 2–8 h; (2) $LiTf_2N$, H_2O, stirred, R.T., 24 h; (3) KPF_6, H_2O, stirred, R.T., 24 h.

ILs possess low vapor pressure and, in contrast to volatile organic solvents, can be used as a reaction medium under vacuum. Due to the latter fact ILs can dilute highly viscous polymer solutions and facilitate the elimination of the byproduct, thus shifting the equilibrium. This work demonstrates a convenient approach to afford ILs with different specific functional groups at the backbone of phenylalkyl pyrrolidinium ([YBPy][X], Y = NO_2, CH_3, F, H; B = benzyl or phenethyl; X = Tf_2N). These ILs reveal excellent thermostabilities and high yields. The polycondensations of bis-β-hydroxyethyl terephthalate (BHET) in these ILs are investigated. High to moderate molecular weights of PET were obtained in shorter time and under relatively mild conditions.

Results and discussion

Synthesis of phenylalkyl pyrrolidinium ionic liquids

The phenylalkyl pyrrolidinium ionic liquids were prepared by the quaternization reaction of *N*-methylpyrrolidine with phenylalkyl bromide at room temperature. Anions (Tf_2N^-, PF_6^-) were introduced by anion exchange reaction from the corresponding phenylalkyl bromide precursors and, subsequently, salts ($LiTf_2N$, KPF_6) in water. The ILs were dried under vacuum at 60 °C for 24 h, and stored at 25 °C before use . The structures of the ILs were confirmed by FTIR, ^{1}H NMR and elemental analysis (see ESI†). A schematic representation of the general structures and synthesis of the pyrrolidinium ILs are shown in Fig. 1 and Scheme 1, respectively.

The size, charge and charge distribution of pyrrolidinium cation are different to the imidazolium cation. The structural variation of the cations in this work influences the ionic interactions and melting points, and thus the consequences of polycondensation in the ILs will be changed.

Effect of molecular structure of IL on melting point

The thermal behaviors of the salts were characterized by differential scanning calorimetry (DSC). The majority of the phenylalkyl pyrrolidinium ILs are solid with melting points in the range of 35–220 °C (ESI, Table S1†). Only two of their Tf_2N^- compounds (**3b** ([4MBPy][Tf_2N]) and **6b** ([4FBPy][Tf_2N])) can be considered as room temperature ionic liquids. Moreover, **3b** and **6b** display no melting points but glass transition temperatures, reflecting a stable supercooling state. It is clear that both cation and anion significantly influence the melting point of the phenylalkyl pyrrolidinium IL.

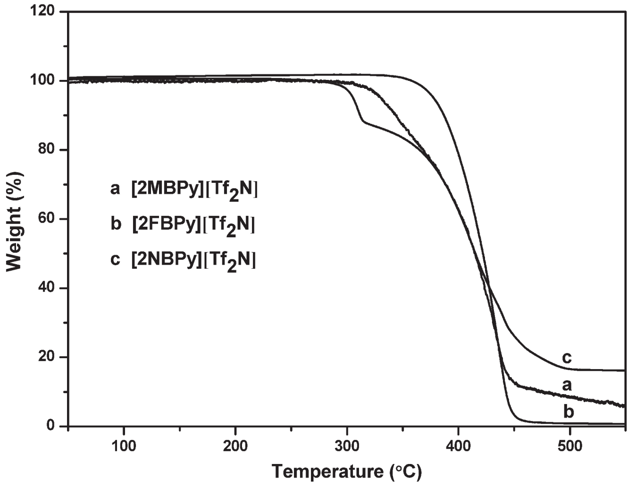


Fig. 2 TGA thermograms of the ILs with different specific functional groups at a heating rate of 10 °C min^{-1} and 50 mL min^{-1} N_2 flow.

It is known that the size, charge, and charge distribution are the main factors that influence the melting point for the cation. The size effect is easily understood because the dominant forces in ionic liquids are the Coulombic and the Van der Waals dispersion interactions. Charge delocalization reduces the charge density, and then diminishes the overall lattice energy. Thus, an important influence of the melting point in phenylalkyl pyrrolidinium ILs is the confined extent of charge delocalization.

The anion plays a crucial role in determining the melting point. The melting point increases in the following order in each case of phenylalkyl pyrrolidinium ILs: $Tf_2N^- < PF_6^-$. The PF_6^- anion is a large, highly symmetrical (O_h), pseudospherical anion. However, the broad extent of charge delocalization and high degree of conformational freedom in the Tf_2N^- anion results in the lower melting point.[40,41]

Thermal stabilities of phenylalkyl pyrrolidinium ionic liquids

The thermal stabilities of phenylalkyl pyrrolidinium ILs were measured by thermogravimetric analysis. Fig. 2 shows the TGA thermograms of ILs with different functional groups. There are four main factors, that is, the nature of the anion, the substituents and their positions on the cation, and the catalyst, that affect the thermal stabilities of the various ionic liquids. The effect of each factor will be discussed in the following.

Anionic constituents of ILs have a great influence on their thermostabilities. The phenylalkyl pyrrolidinium bromides ([YBPy][Br]) are thermally less stable than the corresponding PF_6^- and Tf_2N^- salts. The decomposition temperature (T_d) of phenylalkyl pyrrolidinium IL ([2FBPy][X]) apparently decreases with the following order: [2FBPy][Tf_2N] > [2FBPy][PF_6] > [2FBPy][Br] (ESI, Table S1†). The T_d of the ILs ranges from 290–400 °C except for those with Br^- as the anion. The salts with Tf_2N^- have better thermal stabilities than the PF_6^- salts because PF_6^- is thought to be more basic than Tf_2N^-.

The substituents and their positions on the benzene ring also affect the thermostabilities of these compounds. The highest thermal stability (T_d = 400 °C) is observed for [PhEPy][Tf_2N], which has no functional group on the benzene ring (ESI, Table S1†). In general, introducing specific functional groups into ILs will afford new properties, but will inevitably lower their thermostabilities. The phenylalkyl pyrrolidinium ILs with fluoro- and nitro- substituents possess the highest and lowest values of T_d in the ILs with three types of specific functional groups (Fig. 2; ESI, Table S1†). The positions of the fluorine atom has little influence on the stabilities of the ILs, due to its small volume, electrophilicity and lone-pair electrons' conjugation with the benzene, and thus has a slight effect on the steric hindrance and density of the electron cloud around the benzene ring. Nevertheless, the ILs with bulky groups (methyl and nitro) at the *ortho*-position, which possess a larger steric hindrance, have lower T_d than those with *meta*- and *para*-substituents. There are some turning points about 17% weight loss on the TGA curves of nitrobenzyl pyrrolidinium ILs, which correspond to the mass fraction of methylpyrrolidine in the ILs.

The ILs show degradation in the TGA thermograms above 300 °C, but these temperature ramp experiments are not suitable to describe the degradation during polycondensation. In fact, catalysts may also lead to lower stabilities of ionic liquids, as observed from the isothermal TGA experiments (Fig. 3). A wide variety of ionic liquids may readily retain high thermal stabilities in the processes of heating. However, when the catalyst (EGSb, $Sb(OAc)_3$, or Sb_2O_3) is incorporated into the ILs, the thermal behavior varies sharply according to the categories of anion and catalyst. The ILs with PF_6^- as the anion are not as stable in the presence of catalyst as the ILs with Tf_2N^-, where the mass losses of [3MBPy][PF_6]/catalyst (10–15 wt%) are higher than those of [3MBPy][Tf_2N]/catalyst (<5 wt%). Nevertheless, the thermal stabilities for IL/catalyst apparently follow the order of IL/Sb_2O_3 > IL/EGSb > IL/$Sb(OAc)_3$. The increase of stability of IL/Sb_2O_3 is consistent with the enhanced M_w values in the polycondensation of BHET catalysed by Sb_2O_3 (Table 1, entries 13, 19, 22).

Although phenylalkyl pyrrolidinium ILs have a relatively narrow operating liquid range, the properties of high thermal stability and negligible volatility guarantee applications in polycondensation at high temperature.

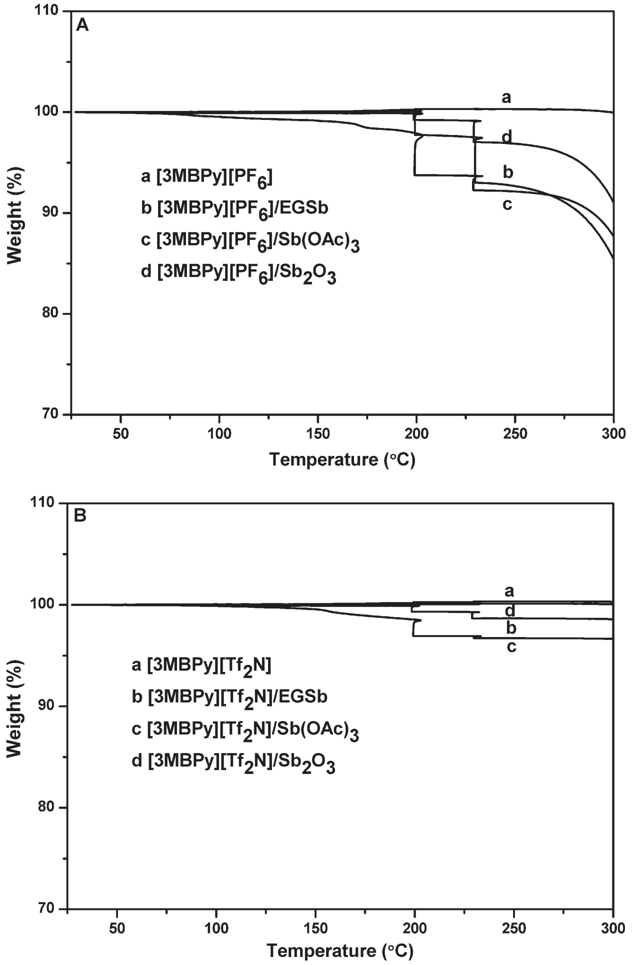


Fig. 3 Isothermal TGA thermograms of ILs with different catalysts under N_2 atmosphere.

Polycondensation of BHET in phenylalkyl pyrrolidinium ionic liquids

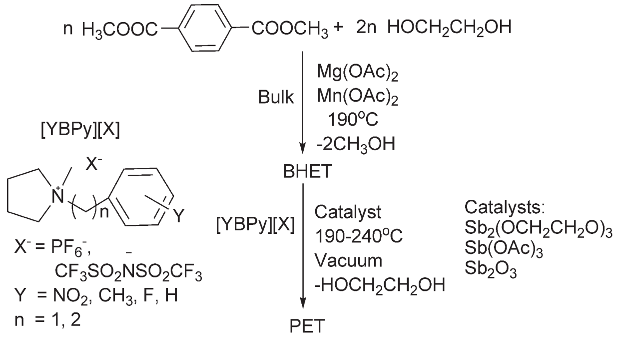
PET was prepared *via* polycondensation which was carried out in two steps with dimethyl terephthalate (DMT) and ethylene glycol (EG): (1) prepolymerization, and (2) polycondensation (Scheme 2). During the prepolymerization step, DMT and EG undergo esterification reactions to form oligomers (BHET) with a degree of polymerization ranging from 4–10. The oligomers react further in phenylalkyl pyrrolidinium IL to obtain high molecular weight PET at the polycondensation step. The results are compared with polycondensation in bulk and the common IL, [BMIM][Tf_2N]. The polycondensation is highly reversible; hence, removal of the small molecules (diol) is essential to afford high molecular weight products. In industry, the polycondensation is carried out at the temperature 280–300 °C and under a high vacuum (10–50 Pa). In this work, the reactions are performed at 190–240 °C and under a vacuum of 500 Pa with a range of catalysts, including EGSb, $Sb(OAc)_3$ and Sb_2O_3. The weight fraction of IL varied from 0 to 90 wt%.

High molecular weight PET ($M_w \approx 1.9 \times 10^4$ g mol^{-1}) is obtained from the polycondensation of BHET in Tf_2N^- ILs at relatively low temperature (230–240 °C) (Fig. 4; Table 1, entry 19). This result is superior to those of the polycondensation of BHET in [PhEPy][Tf_2N], [BMIM][Tf_2N] and bulk (Table 1, entries 41–49), which can be attributed to the influence of aspecific functional groups on the benzene ring. In fact, the M_w value of PET ($M_w \approx 1.9 \times 10^4$ g mol^{-1}, $M_n \approx 1.2 \times 10^4$ g mol^{-1}, PDI = 1.53) is not a very high molecular weight. Presumably, the low molecular weights come from the dilution of reactive groups in the solution polymerization. In order to investigate this speculation, polycondensation of BHET in [2FBPy][Tf_2N] with Sb_2O_3 as a catalyst was carried for a long period (Table 1,

Table 1 Polycondensation of BHET in phenylalkyl pyrrolidinium ILs[a]

Entry	IL	Catalyst	M_w[b]/10^4 (g mol^{-1})	PDI[b]	Yield[c] (%)
1	[2MBPy][PF$_6$]	EGSb	0.42	1.63	ND
2	[2MBPy][PF$_6$]	Sb(OAc)$_3$	0.46	1.63	ND
3	[2MBPy][PF$_6$]	Sb$_2$O$_3$	0.37	1.66	ND
4	[3MBPy][PF$_6$]	EGSb	0.31	1.32	ND
5	[3MBPy][PF$_6$]	Sb(OAc)$_3$	0.34	1.34	ND
6	[3MBPy][PF$_6$]	Sb$_2$O$_3$	0.25	1.23	ND
7	[PhEPy][PF$_6$]	Sb$_2$O$_3$	0.34	1.43	80.8
8	[2MBPy][Tf$_2$N]	EGSb	1.00	1.82	ND
9	[2MBPy][Tf$_2$N]	Sb(OAc)$_3$	1.17	1.71	ND
10	[2MBPy][Tf$_2$N]	Sb$_2$O$_3$	0.75	1.64	ND
11	[3MBPy][Tf$_2$N]	EGSb	1.48	1.47	ND
12	[3MBPy][Tf$_2$N]	Sb(OAc)$_3$	1.58	1.57	ND
13	[3MBPy][Tf$_2$N]	Sb$_2$O$_3$	1.89	1.54	ND
14	[4MBPy][Tf$_2$N]	EGSb	1.03	1.53	84.7
15	[4MBPy][Tf$_2$N]	Sb(OAc)$_3$	1.06	1.44	78.0
16	[4MBPy][Tf$_2$N]	Sb$_2$O$_3$	0.89	1.49	77.3
17	[2FBPy][Tf$_2$N]	EGSb	0.77	1.31	75.2
18	[2FBPy][Tf$_2$N]	Sb(OAc)$_3$	1.20	1.68	76.0
19	[2FBPy][Tf$_2$N]	Sb$_2$O$_3$	1.91	1.59	72.7
20	[3FBPy][Tf$_2$N]	EGSb	1.63	1.49	73.0
21	[3FBPy][Tf$_2$N]	Sb(OAc)$_3$	1.07	1.49	72.0
22	[3FBPy][Tf$_2$N]	Sb$_2$O$_3$	1.76	2.02	74.5
23	[4FBPy][Tf$_2$N]	EGSb	1.09	1.70	69.0
24	[4FBPy][Tf$_2$N]	Sb(OAc)$_3$	1.14	1.82	77.3
25	[4FBPy][Tf$_2$N]	Sb$_2$O$_3$	0.85	1.89	89.0
26	[2NBPy][Tf$_2$N]	EGSb	—[f]	—[f]	—[f]
27	[2NBPy][Tf$_2$N]	Sb$_2$O$_3$	—[f]	—[f]	—[f]
28	[3NBPy][Tf$_2$N]	EGSb	1.06	1.60	74.0
29	[3NBPy][Tf$_2$N]	Sb$_2$O$_3$	1.04	1.64	78.9
30	[4NBPy][Tf$_2$N]	EGSb	—[f]	—[f]	—[f]
31	[4NBPy][Tf$_2$N]	Sb$_2$O$_3$	0.87	1.93	81.3
32[d]	[2NBPy][Tf$_2$N]	EGSb	0.82	1.61	54.0
33[d]	[2NBPy][Tf$_2$N]	Sb(OAc)$_3$	0.86	1.21	70.0
34[d]	[2NBPy][Tf$_2$N]	Sb$_2$O$_3$	0.37	1.44	50.0
35[d]	[3NBPy][Tf$_2$N]	EGSb	0.84	1.13	64.0
36[d]	[3NBPy][Tf$_2$N]	Sb(OAc)$_3$	0.68	1.21	67.0
37[d]	[3NBPy][Tf$_2$N]	Sb$_2$O$_3$	0.65	1.18	60.0
38[d]	[4NBPy][Tf$_2$N]	EGSb	0.98	1.22	65.0
39[d]	[4NBPy][Tf$_2$N]	Sb(OAc)$_3$	1.20	1.18	ND
40[d]	[4NBPy][Tf$_2$N]	Sb$_2$O$_3$	0.87	1.18	75.0
41	[PhEPy][Tf$_2$N]	EGSb	1.30	1.80	77.3
42	[PhEPy][Tf$_2$N]	Sb(OAc)$_3$	1.00	1.84	88.7
43	[PhEPy][Tf$_2$N]	Sb$_2$O$_3$	0.68	1.57	72.8
44	[BMIM][Tf$_2$N]	EGSb	0.54	2.12	70.0
45	[BMIM][Tf$_2$N]	Sb(OAc)$_3$	1.07	2.28	75.0
46	[BMIM][Tf$_2$N]	Sb$_2$O$_3$	1.06	2.14	74.0
47[e]	—	EGSb	0.82	1.62	67.0
48[e]	—	Sb(OAc)$_3$	1.05	1.76	74.7
49[e]	—	Sb$_2$O$_3$	1.04	1.41	80.5
50[g]	[2FBPy][Tf$_2$N]	Sb$_2$O$_3$	0.72	2.38	86.0
51[h]	[2FBPy][Tf$_2$N]	—	0.49	2.26	65.0
52[h]	[3MBPy][Tf$_2$N]	—	0.87	2.05	85.1

[a] General polymerization conditions: BHET (50 wt%), IL (50 wt%) and catalyst (0.1 wt%) reacted at 200 °C for 0.5 h, after the mixture was heated to 230 °C, the pressure was reduced to 1.0×10^3 Pa for 1.5 h and 0.5×10^3 Pa for 1.5 h, finally the temperature was increased to 240 °C at 0.5×10^3 Pa for 0.5 h. [b] Weight-average molecular weight (M_w) and polydispersity index (PDI) measured by GPC calibrated with polystyrene standards. [c] Yield was calculated as the ratio between the purified product's weight and the initial oligoester's weight. ND = Not determined. [d] The reaction temperature was 200 °C. [e] Bulk polycondensation at the same conditions as *a*. [f] Black products and reddish brown substances were generated through the polycondensation, which were not determined. [g] The reaction time was 6 h, *i.e.*, the mixture reacted at 200 °C for 0.5 h, then at 230 °C and 1.0×10^3 Pa for 2.5 h and 0.5×10^3 Pa for 2.5 h, finally the temperature was increased to 240 °C at 0.5×10^3 Pa for 0.5 h. [h] Polycondensation of BHET was performed in ILs without any catalyst. Reaction conditions, see footnote *a*.



Scheme 2 Synthesis of PET by two-step polycondensation in phenylalkyl pyrrolidinium ILs.

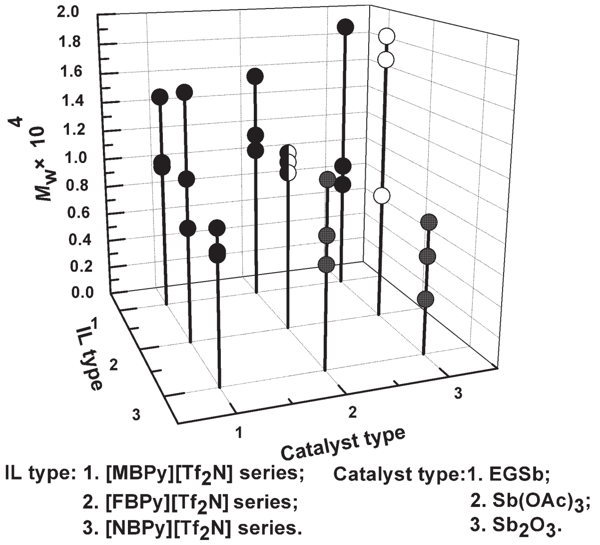


Fig. 4 The dependence of M_w of PET on IL and catalyst. (Three points for each line, for example, (1, 1, M_w), corresponding to the results of three different reactions, those are polycondensations of BHET using EGSb as catalyst in [2MBPy][Tf_2N] (**1b**), [3MBPy][Tf_2N] (**2b**) and [4MBPy][Tf_2N] (**3b**).).

entry 50) and then a low molecular weight of PET ($M_w = 0.72 \times 10^4$ g mol^{-1}, PDI: 2.38, Yield: 86.0%) was obtained. This result indicates that the reaction time does indeed have a crucial effect on the molecular weight of PET. However, in contrast to the dilution of reactive groups, long reaction time and water content of the reaction also favors the degradation of the polymer. The water will act to reduce the equilibrium molecular weight of the polymer. One problem with IL solvents is the difficulty to remove all water, even under the harsh conditions employed during polymerization.

For the polycondensation of BHET in phenylalkyl pyrrolidinium Tf_2N^- ILs, deviations from the molecular weight of PET or the catalytic activity of the catalyst depend on the different specific functional groups on the benzene ring in the ILs. The ILs with methyl- and fluoro- substituents have distinct advantages over those ones with nitro- substituents in the molecular weight of available products under the same conditions (Fig. 4; Table 1, entries 8–31). Practical experience in synthesis shows that there are some constraints on the use of nitrobenzyl pyrrolidinium ILs due to the poor thermostabilities of them. However, it is impossible to rule out the possibility that some fraction of condensation polymers can be obtained in nitrobenzyl pyrrolidinium ILs. In fact, PETs with low molecular weight and broad molecular weight distribution are obtained at 200 °C (Table 1, entries 32–40).

Phase behavior of polycondensation

The evolution of phase behavior for the processes of polycondensation with different ILs ([4FBPy][PF_6] and [2FBPy][Tf_2N]) was recorded on a photographic camera and is displayed in Fig. S2 (ESI†). As the molecular weight of PET gradually increases, phase separation starts to occur. The initially homogeneous sample (Fig. S2 (F)†) becomes opaque and turbid with the reaction proceeding. The mixture of polymer and IL forms a hard solid phase at 240 °C and 500 Pa. Consequently, the effect of stirring on homogenous dispersion is critical at the later stages of polycondensation. A similar observation is obtained in [BMIM][Tf_2N]; however, the mixture of PET/[BMIM][Tf_2N] is hygroscopic and soft because [BMIM][Tf_2N] is a liquid at room temperature. The effects of dilution and viscosity are mainly considered. Dilution is a static effect, and the viscosity influences transportation.

The phase-separated domain structure of the fractured surface was measured by SEM and the observed information is presented in Fig. S3 (ESI†). The networks and bulk aggregates are separated on the edge area adjacent to the bottle (Fig. S3(B, C)†). The networks and aggregates correspond to the PET and IL phases, respectively. In contrast, a homogeneous and continuous phase is formed near to the center. Instead of large holes observed at the edge area, small holes surrounded by viscous mixture of polymer and IL appear at the center in Fig. S3 (D, E†). In other words, formation of a uniform and homogenous morphology will occur if stirred well.

Effect of catalyst on polycondensation

Catalysis plays a critical role in enhancing the rate of the polycondensation reaction. The activity of three types of antimony catalysts is dependent on the anions of the ILs, as reflected in the molecular weight of PET (Table 1). The reddish brown crude product is generated through the polycondensation of BHET in ILs with PF_6^- as the anion. After purifying, yellowish PETs with a relatively low molecular weight are obtained ($M_w < 4.5 \times 10^3$ g mol^{-1}; Table 1, entries 1–7; Fig. S2(D)†), which is lower than the one obtained in bulk polycondensation (M_w: (0.8–1.1) × 10^4 g mol^{-1}; Table 1, entries 47–49). The same trends have been observed in the preparation of aliphatic polyesters in ILs.[35,36] They supposed that the low catalytic activity of the metal cation in IL was caused by the preferential combination of the metal cation with the anion of the IL.

In fact, if only small quantities of water or residues from the preparation of ionic liquids are present as impurities, their thermostability will collapse. Additional evidence of the water contents in samples (ILs, catalysts, and polymer/IL) is provided by Karl Fischer titration at 24 °C (ESI, Table S4†). Under the

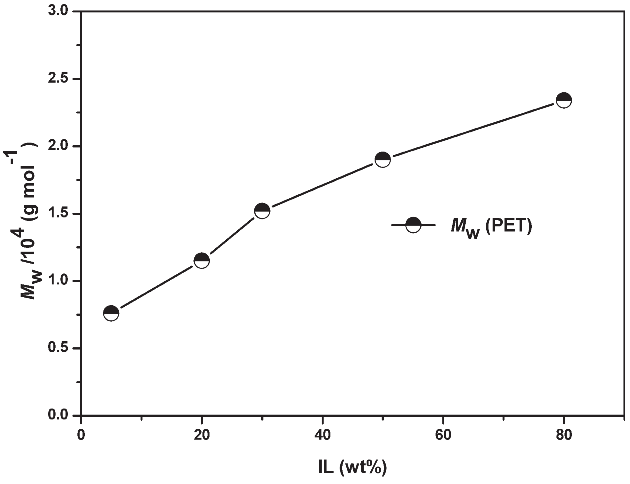


Fig. 5 The dependence of M_w on amount of [4FBPy][Tf$_2$N].

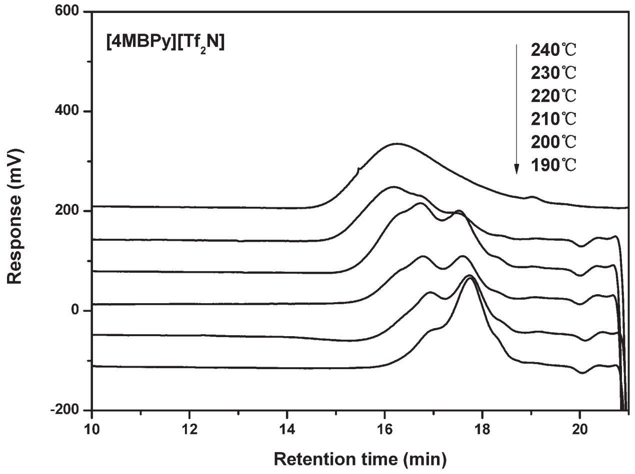


Fig. 6 GPC curves of PET synthesized in [4MBPy][Tf$_2$N] with EGSb as the catalyst at different temperatures.

same drying conditions, the catalyst has the highest water content. ILs with PF_6^- and Tf_2N^- as anions are hydrophobic; however, they can absorb water from the atmosphere. It was also reported that the instability of PF_6^- ILs has been noted due to its hydrolysis in contact with moisture forming volatiles, including HF (CAUTION: HF IS AN EXTREMELY CAUSTIC LIQUID AND VAPOR AND EXTREME CARE SHOULD BE TAKEN DURING HANDLING), POF_3, *etc.*, which can dissolve glassware.[42] The difference in performances are more significant for ILs with PF_6^- and Tf_2N^- as counterions. In terms of the thermal properties, it is reasonable to suppose that there are some kind of interactions between the IL and catalyst, and water, probably as the important forces effective in this process.

Interest in phenylalkyl pyrrolidinium ionic liquids will increase if the polycondensation of BHET was performed in ILs without any catalyst for comparison. The results of these cases reveal condensation polymers with molecular weights (0.5–0.9) × 10^4 g mol^{-1} (Table 1, entries 51–52), leading to the conclusion that the polycondensation can be truly considered as green.

Effect of amount of IL on polycondensation

Polycondensation of BHET in [4FBPy][Tf$_2$N] catalyzed by $Sb(OAc)_3$ was chosen as a model system to quantitatively demonstrate the effect of amount of IL (see ESI, Table S2†). The variation of M_w of PET *versus* the concentration of IL is plotted in Fig. 5. The M_w of PET increases with the increase of IL, because the mobility of PET chains and the probability of collision of the terminal groups on BHET are enhanced with the increased amount of IL. It also favors the polycondensation processes, which require eliminating the small molecules at high temperature, due to the diluting abilities of ILs.

Effect of temperature on polycondensation

The temperature is an important influence parameter in the process of polycondensation. The reaction is diffusion-controlled at the later stage of polycondensation due to high melt viscosity. Thus it requires a high temperature to ensure the product is in a molten state. However, this generates side reactions, like the degradation of the PET chains. It is noted that ILs already have demonstrated their ability to decrease reaction temperature in polycondensation processes.[43]

In this work, the polycondensations of BHET in [4MBPy][Tf$_2$N] catalyzed by EGSb at different temperatures were investigated (Fig. 6; ESI, Table S3†). The reaction temperature was controlled between the glass transition temperature and the melting point of PET, which is much lower than the temperature of melt polycondensation and limits thermal degradation. As can be seen in Fig. 6, the M_w of PET reaches the maximum value at 230 °C. The molecular weight distributions (MWDs) of PET become increasingly bimodal and the shoulder peaks at the low molecular weight part increase with decreasing reaction temperature. Lower M_w values are attributed to the decrease of monomer concentration, which is caused by the conversion of BHET forming polymer in the IL.

Isolation and reuse of ILs

It is imperative that ILs can be recovered when they are serving as reaction media in green chemistry processes. Based on the difference of solubility between PET and phenylalkyl pyrrolidinium ILs, PET can be isolated by simple ethanol extraction, which is considered as a convenient and environmentally friendly process. The IL can be efficiently recovered from ethanol.

Most of the recovered ILs are deep color solids or viscous liquids. As can be seen from the FTIR spectra (see ESI, Fig. S1†), the absorption peak observed at 830 cm^{-1}, which is assigned to the P–F bond of PF_6^- in recovered ILs, disappeared. It indicates that the P–F bond decomposed during the polycondensation or isolation processes. The PF_6^- anion is subject to hydrolysis in the presence of water traces even at 70 °C.[42] During the polycondensation process ethylene glycol is evolved, while during the prepolymerization the traces of methanol could still remain in BHET even after its drying. Additionally ethanol is used as the solvent for the separation of the polymer from the

Table 2 The polycondensation of BHET in recycled ILs[a]

Entry	IL	Catalyst	Temperature (°C)	$M_w/10^4$ (g mol^{-1})	PDI	Yield (%)
1	[3NBPy][Tf_2N]	EGSb	200	0.62[b]	1.13	ND[c]
2	[4FBPy][Tf_2N]	EGSb	200	0.81[b]	1.19	76.3
3	[4MBPy][Tf_2N]	EGSb	200	0.50[b]	1.65	77.5

[a] Polymerization conditions, see footnotes of Table 1. Only the reaction temperature was changed as follows: BHET, IL and catalyst reacted at 180 °C for 0.5 h, after the system was heated to 190 °C, the pressure was reduced to 1.0×10^3 Pa for 1.5 h and 0.5×10^3 Pa for 1.5 h, finally the temperature was increased to 200 °C under 0.5×10^3 Pa for 0.5 h. [b] Bimodal distribution. [c] ND = Not determined.

ionic liquid. In general, any of the mentioned factors can cause the hydrolysis of PF_6^- ionic liquids.

However, the Tf_2N^- ILs have less changes before and after use. For this study, the content of catalyst is determined by inductively coupled plasma spectrometry. It is demonstrated that the product is formed with 0.12 μg mL^{-1} Sb catalyst after separation from the IL. A decrease of catalyst content is observed for the recycled IL ([3MBPy][Tf_2N]: 0.05 μg mL^{-1}). Consequently, a new portion of Sb catalyst was added in the polycondensation performed in recycled IL. PETs with relative low molecular weight and bimodal distribution are obtained at low reaction temperature (Table 2).

Conclusion

In summary, a series of novel phenylalkyl pyrrolidinium ILs were synthesized and have been demonstrated to be reaction media for the preparation of PET with relatively high molecular weight ($M_w \approx 1.9 \times 10^4$ g mol^{-1}). The ILs with specific functional groups showed high thermostabilities. The effects of the activity of antimony catalysts, amount of IL and reaction temperature were investigated. All ILs could be easily recycled and reused after simple purification except for the PF_6^- ILs.

The high and moderate molecular weights, green reaction media, as well as manipulative simplicity in relative mild conditions make this process a valuable and environmentally friendly alternative to the currently available methods for the preparation of PET in industry.

Experimental section

Materials

N-Methylpyrrolidine (99%, Dalian Rich Fortune Chemicals Co., Ltd, China), lithium bis(trifluoromethylsulfonyl)imide ($Li(CF_3SO_2)_2N$, ≥99%, TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan), potassium hexafluorophosphate (KPF_6, 99%, Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China), 2-phenethyl bromide (98%, Alfa Aesar China) were used as received. Benzyl bromides (97%) were purchased from Tianjin Shentuo Jingyi Chemical R & D Center (Tianjin, China) and used without further purification. Ethylene glycol (AR, Beijing Chemical Plant, Beijing, China) was distilled under reduced pressure. Dimethyl terephthalate (DMT, CP, Beijing Chemical Plant, Beijing, China) was recrystallized in methanol before used. Antimony glycolate ($Sb_2(OCH_2CH_2O)_3$, EGSb) and antimony acetate ($Sb(OAc)_3$) were prepared according to procedures in the literatures.[44–46] All catalysts used were dried at 60 °C for 6 h. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf_2N]) was prepared according to literature procedures.[47]

Methods

All compounds were characterized by ^1H NMR. Nuclear magnetic resonance (NMR) spectra were taken on an Avance Brucker-400 MHz, and chemical shifts of NMR were reported in parts per million (ppm, δ). Splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). FTIR (cm^{-1}) spectra were recorded on an Omnic AVATAR 360, Nicolet, USA. The intensity of the infrared absorptions and reflections were designated as vs (very strong), s (strong), m (medium), w (weak), br (broad). Elemental analyses were obtained on a Vario El elemental analyser (Elementar). Thermogravimetric analysis (TGA, ZRY-2P, Balance Instrument Factory, Shanghai Precision Scientific Instrument Co., Ltd, China) was carried out in an Al_2O_3 pan from 25 to 600 °C at a heating rate of 10 °C min^{-1} under 50 mL min^{-1} N_2 flow. Decomposition temperature (T_d) was obtained *via* TGA and defined as the temperature at which a 10% weight loss was observed. Isothermal TGA measurements were conducted from 25–200 °C at a heating rate of 10 °C min^{-1} and held at 200 °C for 30 min, then heated to 230 °C at 10 °C min^{-1} and isothermally for another 30 min, finally brought to 300 °C at 10 °C min^{-1}. Unless otherwise noted, this was done under 50 mL min^{-1} N_2 flow with open Al_2O_3 pans. A Mettler DSC1 (STAR^e System) differential scanning calorimeter, operated under 40 mL min^{-1} nitrogen flow and equipped with a liquid nitrogen cooling accessory, was used to detect the evolution of heating or cooling during the phase transition. Temperature and heat flow were calibrated by indium standards. A dry and constant flow of nitrogen was maintained in order to eliminate thermal gradients and ensure the validity of the calibration standard from sample to sample. Each sample was heated from 25 to 250 °C at 10 °C min^{-1} and maintained at this temperature for 5 min to allow the complete melting of the crystallites, followed by cooling to −100 °C, then heating again up to 250 °C at 10 °C min^{-1}. The glass transition temperature (the midpoint temperature of the heat capacity change, T_g) was determined from the DSC thermograms. The values of enthalpy and entropy were normalized with respect to the amount of IL. The samples of PET (3.0 mg) were dissolved in *o*-chlorophenol (0.3 mL) at 95–105 °C for 15 min and diluted with chloroform to give a final concentration of 1.2 mg mL^{-1}. The solution was filtered through a syringe filter before injection. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (PLGPC 50, Polymer Laboratories Corporation) using chloroform as eluant at a flow rate of 1.0 mL min^{-1} at 40 °C. Water content was analyzed by Karl Fischer titration technique (Mettler Toledo DL38 KF titrators) at 24 °C. The sample was dissolved in methanol and titrated. Inductively coupled plasma (ICP) data were collected on a JY Ultima ICP spectrometer (France). The microscopic image was recorded on a HITACHI S-4800 scanning electron microscope.

Preparation of phenylalkyl pyrrolidinium ionic liquids

1-Methyl-1-(2-methylbenzyl)pyrrolidinium bromide [2MBPy][Br] (1a). To a stirred solution of *N*-methylpyrrolidine (4.26 g, 50 mmol) in ethyl acetate (50 mL) was slowly added 2-methylbenzyl bromide (9.25 g, 50 mmol) under nitrogen atmosphere. The mixture was stirred for 8 h at room temperature, and then filtered to remove the solvent. The crude product was washed with ethyl acetate several times, and dried under vacuum at 60 °C for 24 h to provide 1-methyl-1-(2-methylbenzyl)pyrrolidinium bromide as a white solid.

Yield: 12.98 g (96.1%); T_d: 210 °C; Found: C, 57.73%, H, 7.34%, N, 5.15%; Calc. for $C_{13}H_{20}NBr$ (269.08): C, 57.78%, H, 7.46%, N, 5.18%; ^{1}H NMR (400 MHz, D_2O): δ = 7.34–7.18 (br, 4H, C_6H_4), 4.45 (s, 2H, $NCH_2C_6H_4$), 3.47–3.32 (br, 4H, $NCH_2CH_2CH_2CH_2$), 2.82 (s, 3H, NCH_3), 2.30 (s, 3H, $C_6H_4CH_3$), 2.07–2.06 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3021 (m, ν_{Ar-H}), 2998 (s), 2963 (s), 2888 (s), 2832 (m, ν_{C-H}), 1603 (m), 1467 (s), 1455 (s), 1389 (m), 1158 (m, ν_{C-N}), 898 (s), 886 (s), 876 (s), 829 (m), 783 (s), 755 (s), 732 (m), 702 (m) cm^{-1}.

1-Methyl-1-(2-methylbenzyl)pyrrolidinium bis(trifluoromethylsulfonyl)imide [2MBPy][Tf$_2$N] (1b). To a stirred solution of [2MBPy][Br] (2.69 g, 10 mmol) in deionized water (20 mL) was slowly added an aqueous solution of LiTf$_2$N (2.87 g, 10 mmol) at room temperature for 24 h under a nitrogen atmosphere. [2MBPy][Tf$_2$N] was separated from the aqueous solution by filtration, washed with water several times, and dried under vacuum at 60 °C for 24 h to provide the title product as a white solid.

Yield: 4.14 g (88.1%); T_d: 340 °C; Found: C, 38.26%, H, 4.44%, N, 5.85%; Calc. for $C_{15}H_{20}N_2S_2O_4F_6$ (470.08): C, 38.30%, H, 4.28%, N, 5.95%; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.46–7.30 (br, 4H, C_6H_4), 4.59 (s, 2H, $NCH_2C_6H_4$), 3.45 (br, 4H, $NCH_2CH_2CH_2CH_2$), 2.86 (s, 3H, NCH_3), 2.42 (s, 3H, $C_6H_4CH_3$), 2.08 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm. IR (KBr pellet): 3073 (w), 3030 (w), 2994 (m), 1480 (m), 1465 (m), 1352 (s, $\nu_{S=O}$), 1217 (s), 1139 (s), 1055 (s, ν_{C-F}), 928 (m), 911 (m), 790 (m), 779 (m), 762 (w), 752 (m), 740 (m), 616 (s), 570 (s), 514 (s) cm^{-1}.

1-Methyl-1-(2-methylbenzyl)pyrrolidinium hexafluorophosphate [2MBPy][PF$_6$] (1c). To a stirred solution of [2MBPy][Br] (2.69 g, 10 mmol) in deionized water (20 mL) was slowly added aqueous solution of KPF$_6$ (1.84 g, 10 mmol) at room temperature under nitrogen atmosphere. [2MBPy][PF$_6$] was separated from aqueous solution by filtration, washed with water several times, and dried under vacuum at 60 °C for 24 h to provide the title product as a white solid.

Yield: 2.68 g (80.0%); T_d: 320 °C; Found: C, 46.55%, H, 5.93%, N, 4.12%; Calc. for $C_{13}H_{20}NPF_6$ (335.12): C, 46.57%, H, 6.01%, N, 4.18%; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.48–7.28 (br, 4H, C_6H_4), 4.59 (s, 2H, $NCH_2C_6H_4$), 3.50–3.42 (br, 4H, $NCH_2CH_2CH_2CH_2$), 2.86 (s, 3H, NCH_3), 2.42 (s, 3H, $C_6H_4CH_3$), 2.10–2.08 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3079 (m), 3024 (m, ν_{Ar-H}), 2987 (m), 2936 (m, ν_{C-H}), 1608 (w), 1470 (s), 1385 (m), 1295 (w), 1218 (w), 834 (s, ν_{P-F}), 557 (s) cm^{-1}.

Preparation of bis-β-hydroxyethyl terephthalate (BHET)

Into a 250 mL three-necked flask, ethylene glycol (19.22 g, 0.31 mol) was added into stirred dimethyl terephthalate (29.14 g, 0.15 mol) at 110 °C under nitrogen atmosphere. The catalyst Mn(OAc)$_2$ and Mg(OAc)$_2$ were added to the mixture at 190 °C. Methanol was distilled off after 30 min at the same temperature. The reaction was kept at 190 °C for 6 h and quenched by cooling to room temperature. The product was smashed into bits and dried at 60 °C for 12 h before being used in subsequent polycondensation.

Typical synthesis of PET

BHET (1.5 g, 50 wt%), IL (1.5 g, 50 wt%) and catalyst (0.0015 g, 0.1 wt%) were charged into a dry vial. The mixture was degassed by three consecutive vacuum–nitrogen cycles. The reaction was performed in an oil bath thermostated at a prescribed temperature and pressure. The polycondensation was conducted at 200 °C for 0.5 h, after that the mixture was heated to 230 °C, the pressure was reduced to 1.0×10^3 Pa for 1.5 h and 0.5×10^3 Pa for another 1.5 h, finally the temperature was increased to 240 °C at 0.5×10^3 Pa for 0.5 h. The polymerization was terminated by adding nitrogen and cooling to room temperature. The purified PET was obtained by Soxhlet extraction with ethanol for 12 h to afford white solid, and the ILs were recycled by rotary evaporation to remove the solvent.

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