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Investigation of Physicochemical Properties of Lactam-Based Brønsted Acidic Ionic Liquids

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Novel lactam-cation-based Brønsted acid ionic liquids (ILs) were prepared through a simple and atom-economic neutralization reaction between a lactam, such as caprolactam and butyrolactam, and a Brønsted acid, HX, where X is BF_4^-, CF_3COO^-, $phCOO^-$, $ClCH_2COO^-$, NO_3^-, or $H_2PO_4^-$. The density, viscosity, acidic scale, electrochemical window, temperature dependency of ionic conductivity, and thermal property of these ILs were measured and investigated in detail. The results show that protonated caprolactam tetrafluoroborate (CPBF) has a relatively strong acidity with −0.22 of Hammett acidic scale H_0 and caprolactam trifluoroacetate (CPTFA) and pyrrolidonium trifluoroacetate (PYTFA) ILs possess very low viscosities, that is, 28 cP and 11 cP, respectively. An investigation of thermal property showed that a wide liquid range (up to −90 °C), moderate thermal stability (up to 249 °C for 10% of decomposition), and complex polymorphism were observed in these ILs. In comparison to imidazolium-cation-based ILs, the lactam-cation-based Brønsted acid ILs have a relatively lower cost, lower toxicity, and comparable ion conductivity and heat storage density (more than 200 MJ/m^3). They have wide applicable perspectives for fuel cell devices, thermal transfer fluids, and acid-catalyzed reaction media and catalysts as replacements of conventional inorganic acids.

Introduction

Room-temperature ILs have gained recognition as environmentally benign alternatives to volatile organic solvents and have been used for many reactions in recent years because they possess several peculiar physicochemical properties such as wide liquid range, negligible vapor pressure, high thermal stability, and good solvating ability for a wide range of substrates and catalysts.[1−5] Developing new kinds of room-temperature ILs and finding new physicochemical properties for potential application have been the hot topics in the field of current IL research.

Brønsted acidic task-specific ILs, for example, dialkylimidazolium salts with a side chain containing a −SO₃H group, have been reported and used as catalysts and/or media instead of inorganic acids in many conventional acid-catalyzed reactions, such as olefin oligomerization,[6] etherification,[7] esterification,[8] and Friedel−Crafts alkylation.[9] Lately, *N*-protonated 1-alkylimidazolium salts were prepared by several research groups through acid−base neutralization.[10,11] He et al. used *N*-protonated 1-methylimidazolium tetrafluoroborate as a Brønsted acid catalyst successfully in esterification[12] and carbonyl protection.[13] In addition, the Brønsted acid−base ILs prepared from imidazole and bis(trifluoromethanesulfonyl)amide could be used as a proton-conducting nonaqueous electrolyte in fuel cell devices.[14] However, the main disadvantages of imidazolium-based ILs have been their relatively higher cost and toxicity[15] in general chemical applications. Therefore, the development of lower cost and intrinsic lower toxicity room-temperature ILs is highly desired. It was reported that amide could react with alkyl halide to form tetraalkylammonium salts,[16,17] but such an amide is not easily available in large amounts and is very expensive. In addition, the formed ILs have very low thermal decomposed temperatures or higher melting points.

Lactam, especially ϵ-caprolactam and γ-butyrolactam (i.e., 2-pyrrolidone), which is relatively cheaper, has an intrinsic lower toxicity, and is easily available in large amounts from industry, is a kind of amine derivative that could be quaternized to form a new kind of cation of IL. The additional carbonyl groups in the lactam might lead to specific functions when these lactam-based ILs are used as media or solvents. Moreover, they are relatively cheaper and more environmentally friendly in comparison to imidazolium-based ILs. Recently, the preparation of caprolactam ILs was reported by our group,[18] but the used lactam was limited to caprolactam and there was no other lactam involved. Moreover, the detailed characterization of physicochemical properties of lactam-based Brønsted acidic ionic liquids have not been reported yet.

Herein, we report our recently developed Brønsted acidic functionalized ILs through the preparation of lactam-based salts containing BF_4^-, CF_3COO^-, $phCOO^-$, $ClCH_2COO^-$, NO_3^-, and $H_2PO_4^-$ anions through a simple neutralization reaction between a lactam, such as caprolactam and butyrolactam, and a Brønsted acid and their corresponding Brønsted acidity and physicochemical properties were characterized and investigated in detail. The effect of the size of the cation on the properties was also discussed.

Experimental Section

Materials. All reagents used in this study were obtained from Tianjin Chemical Reagent Corporation Ltd and were used without further purification except for butyrolactam. The latter was obtained from Merk with purity of 99.0%.
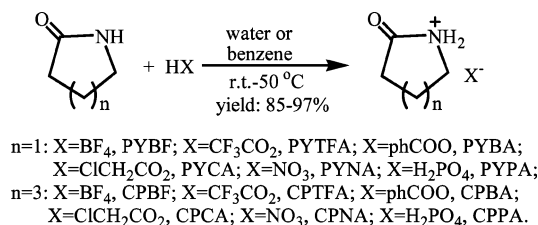
Analysis and Measurement. The ¹H and ¹³C NMR spectra were recorded on a Bruker AMX FT 400-MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). Electrospray ionization mass spectra were recorded

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SCHEME 1: Preparation of Lactam-Based ILs

n=1: X=BF$_4$, PYBF; X=CF$_3$CO$_2$, PYTFA; X=phCOO, PYBA;
X=ClCH$_2$CO$_2$, PYCA; X=NO$_3$, PYNA; X=H$_2$PO$_4$, PYPA;
n=3: X=BF$_4$, CPBF; X=CF$_3$CO$_2$, CPTFA; X=phCOO, CPBA;
X=ClCH$_2$CO$_2$, CPCA; X=NO$_3$, CPNA; X=H$_2$PO$_4$, CPPA.

on a Bruker Daltonics APEX II 47e FTMS. The density was examined by the weight method at 25 °C. The viscosity was measured by a capillary viscometer in a water bath at a constant temperature of 25 °C. The ion conductivity was measured by using a DDS-11A digital conductivity-meter at varied temperatures. The cyclic voltammetry curve was detected by using a CHI 660A Electrochemical Work Station at room temperature with a 3-mm-diameter platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The measurement of the Brønsted acidic scale of ILs was conducted on an Agilent 8453 UV−vis spectrophotometer with a basic indicator. Thermal analysis and temperature-dependent phase behavior were examined in the circular range of −150 to 110 °C by using a Mettler Toledo DSC822^e Differential Scanning Calorimeter with scan rate of 10 °C/min under N$_2$ atmosphere. The samples for DSC measurements were tightly sealed in Al pans. The glass transition temperature (T_g) and melting point (T_m) were recorded as the midpoint of the glass transition and the onset of the melting transition of the DSC curve, respectively. The decomposition temperature (T_d) was recorded with 10% of mass loss by using a Pyris Diamond Perkin-Elmer TG/DTA with scan rate of 20 °C/min under N$_2$ atmosphere. The samples for TG/DTA measurements were sealed tightly in Al$_2$O$_3$ pans. A sapphire disk (Al$_2$O$_3$) was used as the standard substance to determine the heat capacity of the IL samples in the DSC measurement.

General Procedures for the Preparation of Lactam-Based ILs. The preparation of lactam-based ILs and their abbreviations were illustrated in Scheme 1. In a typical experiment, the preparation of Brønsted acidic caprolactam trifluoroacetate (CPTFA) was regarded as an example and others were as similar.

Benzene (30 mL) was added to a 100-mL flask containing 11.32 g of ε-caprolactam (0.1 mol) and stirred. Then, 11.40 g of trifluoroacetic acid (0.1 mol) was dripped slowly into the flask within ca. 30 min in an ice bath. The reaction lasted for another 4 h at room temperature. Benzene was removed under reduced pressure and further dried at 90 °C under 1−5 mmHg for 1 h. ^{1}H NMR (CDCl$_3$): 1.65−1.82 (m, 6H), 2.51 (q, J = 5.2, 2H), 3.27 (q, J = 5.6, 2H), 8.06 (s, 1H), 15.89 (s, 1H). (D$_2$O): 1.22−1.41 (m, 6H), 2.14 (q, J = 4.8, 2H), 2.90 (q, J = 5.2, 2H). ^{13}C NMR (CDCl$_3$): 22.74, 28.86, 30.25, 42.91, 115.23 (q, CF$_3$, J = 288.0), 160.99, 181.02.

Results and Discussion

All of the lactam-based ILs were prepared with high yields of 85−97%. They are moisture stable. Among of them, CPBF, CPTFA, PYBF, and PYTFA are colorless to brown liquids with excellent fluidity at room temperature and can be miscible with water, whereas the others are white to fawn solids with melting points of less than 64 °C (see DSC results) and have excellent solubility in water. Although all of these ILs are insoluble in diethyl ether and benzene, they are miscible with many polar organic solvents, such as methanol, acetonitrile, and acetone, as are typical imidazolium-cation-based ILs.

TABLE 1: Density, Viscosity, Electrochemical Window, and Ionic Conductivity of Lactam-Based ILs[a]

ILs	density (g/mL)	viscosity (cP)	electrochemical window (V)	ionic conductivity (S/m)
CPBF	1.33	503	2.0	7.31×10^{-2}
CPTFA	1.24	28	2.1	3.83×10^{-2}
PYBF	1.46	350	2.2	8.39×10^{-2}
PYTFA	1.32	11	2.4	1.44×10^{-1}

[a] Density, viscosity, conductivity, and electrochemical window were measured at 25 °C.
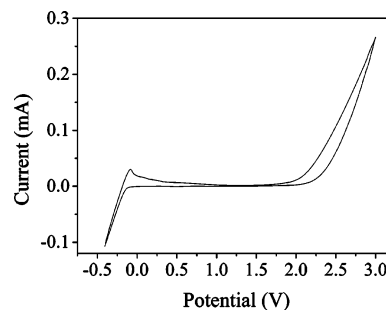

Figure 1. Cycle voltammogram of PYTFA.

Density and Viscosity. The densities and viscosities of CPBF, CPTFA, PYBF, and PYTFA ILs were measured and listed in Table 1. It can be seen that both cations and anions have a significant effect on their physicochemical properties. The ILs containing BF$_4^-$ possess higher densities and viscosities than those of ILs containing the CF$_3$COO$^-$ anion. As for the same anion, with the increase of the ring number of the cation, the density decreased, whereas the viscosity apparently increased. The size increase of the cation may lead to the interaction modification between the cation and the anion. In comparison to 1-butyl-3-methylimidazolium-based ILs, the lactam-based ILs have higher densities, for example, 1.33 g/mL and 1.24 g/mL at 25 °C for CPBF and CPTFA in comparison to 1.208 g/mL of BMImBF$_4$[19] and 1.209 g/mL of BMIm[CF$_3$COO][20], respectively. It is worth noting that lactam-based ILs with CF$_3$COO$^-$ anions exhibited lower viscosities (less than 30 cP at 25 °C), particularly for PYTFA, 11 cP of viscosity was achieved, which could be comparable as the most commonly used organic solvent.

Electrochemical Window. The electrochemical stability of the above-mentioned four ILs was analyzed with cyclic voltammetry at room temperature. From the results (Table 1), it can be seen that the lactam-based ILs were electrochemically stable in the potential range from −0.2 to 2.2 V versus Ag/AgCl, that is, the electrochemical windows were ca. 2.0−2.4 V. Such electrochemical windows are not as wide as those of 1-butyl-1-methylpyrrolidinium TFSA salts (5.5 V)[21] and 1-butyl-3-methylimidazolium trifluoroacetate (3.8 V),[20] particularly in the reduction region because of the presence of active H$^+$, which means the reduction stability is not very good. A typical cyclic voltammogram of PYTFA is shown in Figure 1. An irreversible oxidation was observed at −0.2 V, which may result from the oxidation of a trace amount of a precursor γ-butyrolactam compound.

Ionic Conductivity. The ionic conductivities of CPBF, CPTFA, PYBF, and PYTFA ILs were determined in the range of 15−90 °C under vacuum (5−10 mmHg). The data at 25 °C (Table 1) show that PYTFA possesses the higher ionic conductivity (0.144 S/m, whereas 0.1 S/m for BMIm[CF$_3$COO][20]). This might be attributed to lower viscosity and smaller cation size, which may improve the rate of ion mobility.
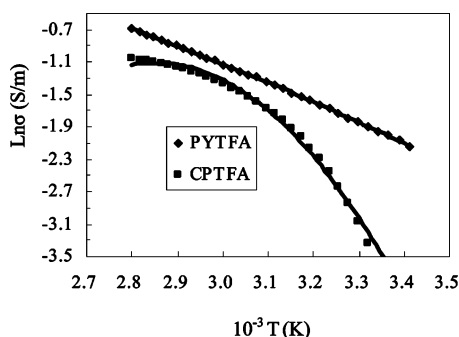
Figure 2. Arrhenius plots of ion conductivity for PYTFA and CPTFA.

TABLE 2: VTF Equation Parameters for Ion Conductivity Data $\sigma = \sigma_0 \exp[-B/(T - T_0)]$

ionic liquids	$\sigma_0/\text{S}\cdot\text{m}^{-1}$	B/K	T_0/K	R^2
CPTFA	0.66	44.54	287.07	1.000
PYTFA	18.28	811.09	132.18	0.995

Unexpectedly, the ionic conductivity of CPBF is close to that of PYBF, whereas the ionic conductivities of CPTFA and PYTFA have significant differences, this is probably attributed to integrative factors, such as the structure of the cation and anion, hydrogen bond interactions, diffusion coefficient, and viscosity. To further investigate the temperature dependency of the ionic conductivity, PYTFA and CPTFA having relatively lower viscosity were studied and their Arrhenius plots are depicted in Figure 2. The relationships of temperature dependency of the ionic conductivity were greatly different, that is, a linear line for PYTFA while an apparent convex curved-profile for CPTFA was observed, respectively. The temperature dependency of the ionic conductivity can be fitted with Vogel−Tamman−Fulcher (VTF) eq 1[22]

$$\sigma = \sigma_0 \exp[-B/(T - T_0)] \qquad (1)$$

where σ_0 (S/m), B (K), and T_0 (K) are constant parameters. The solid lines in Figure 2 are drawn based on the VTF equation and the best-fit σ_0 (S/m), B (K), and T_0 (K) parameters given in Table 2. When the cation pyrrolidonium was replaced with the more bulky caprolactam cation, the VTF B and σ_0 parameters of CPTFA become smaller, whereas parameter T_0 becomes larger than those of PYTFA. These results show that the VTF parameters have a great effect on the ionic conductivity of the two ILs.

Acidity Characterization. The measurement of the Brønsted acidic scale of these lactam-based ILs was conducted on an Agilent 8453 UV−vis spectrophotometer with a basic indicator according to the literature reported previously.[23] With the increasing acidic scale of the acidic ILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas the protonated form of the indicator could not observed because of its small molar absorptivity and its location, so the $[\text{I}]/[\text{IH}^+]$ (I represents indicator) ratio could be determined from the measured absorbance differences after addition of acidic lactam-based IL, and then the Hammett function, H_0, is calculated by using eq 2. This value can be regarded as the relative acidity of the ILs.

$$H_0 = pK_a(\text{I}) + \log([\text{I}]/[\text{IH}^+]) \qquad (2)$$

Under the same concentration of methyl yellow (7.5 mg/l, $pK_a = 3.3$) and acidic lactam-based IL (80 mmol/l) in dichloromethane, we determined the H_0 of the ILs. When the acidity of the ILs was too strong to differentiate them from one another,
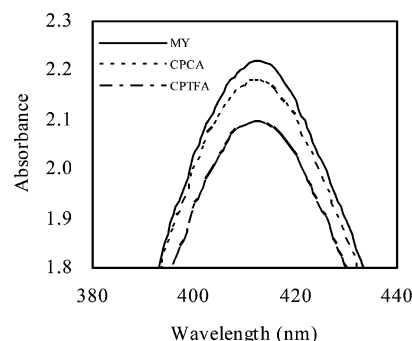

Figure 3. UV-vis absorbances of CPCA and CPTFA.

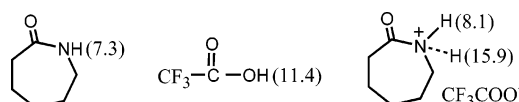**SCHEME 2: Chemical Shifts (ppm) of Active Hydrogens of CPTFA and Its Raw Materials**

TABLE 3: Heat Capacity (C_p) and Heat Storage Density (D_h)[a] for Lactam-Based ILs and BMImBF4

ILs	CPBF	CPTFA	PYBF	PYTFA	BMImBF4
C_p, 25 °C (J/g/°C)	1.57	1.60	1.58	1.61	1.63
D_h, $\Delta T = 100$ °C (MJ/m³)	210.4	201.6	230.7	210.9	194.9[24]

^{a} $D_h = \rho \cdot C_p \cdot \Delta T$.

we could use another weaker basic indicator, such as 4-phenylazodiphenylamine ($pK_a = 1.5$) and 2-nitrophenylamine ($pK_a = -0.2$), to examine it. Ultimately, we obtained the acidity order of seven lactam-based ILs with the following H_0 values: CPBF (-0.22) > PYBF (0.91) > CPNA (2.08) > CPTFA (3.35) > PYTFA (3.48) > CPCA (5.04) > CPBA (6.07), suggesting that the Brønsted acidity of CPBF was relatively stronger and the Brønsted acidity of the lactam-based ILs was apparently dependent upon the structure of the cation and anion. The typical absorption spectra of CPCA, CPTFA, and pure methyl yellow (MY) in dichloromethane using MY as the indicator are shown in Figure 3.

The acidity of the lactam-based ILs could also be illustrated by their ${}^1\text{H}$ NMR characterizations. From the ${}^1\text{H}$ NMR spectra, it was found that all of the ILs had two active hydrogens that shifted downfield at different degrees depending on the various anions; for example, two active H shifted from 7.3 to 8.1 ppm and 11.4 to 15.9 ppm, respectively, for CPTFA in comparison to the corresponding H in pure caprolactam and CF₃COOH (Scheme 2), indicating that such an acidic H did not bond covalently to N but dissociated around caprolactam and CF₃COO⁻. However, electrospray ionization MS (ESI⁺) of CPTFA showed that the m/z value of the cation was 114.0910 versus 114.0913 for the calculated value (C₆H₁₂NO), indicating that caprolactam could be protonated easily and the N-protonated caprolactam cation was really formed.

Heat Capacity and Heat Storage Density. Heat capacity must be known in order to calculate the sensible heat storage density of the ILs. Analysis of the heat flow at temperatures at which no enthalpy or glass transitions occur gives the heat capacity directly. The heat capacities of CPBF, CPTFA, PYBF, PYTFA, and BMImBF₄ (for the purpose of comparison) ILs were measured with sapphire as the reference substance in the temperature range from -40 to 40 °C, and the heat capacities (C_p) and sensible heat storage densities (D_h) for these ILs are summarized in Table 3. It can be seen that the heat capacities for the lactam-based ILs are slighly lower than that for

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TABLE 4: Thermal Stability and Phase Behavior of Lactam-Based ILs

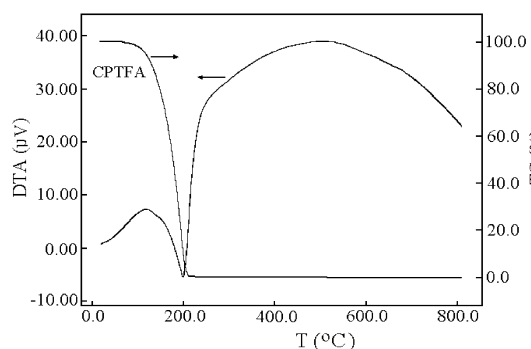| ILs	T_d (°C)	T_c (°C)	T_f (°C)/ ΔH_f (J/g)	T_g (°C)/ $\Delta C_p{}^a$ (J/g/°C)	$T_1{}^b$(°C)/ ΔH_1 (J/g)	$T_2{}^b$ (°C)/ ΔH_2 (J/g)	T_m (°C)/ ΔH_m (J/g)
CPBF	239			−74/0.190			
CPTFA	135	−111		−73/0.278			
CPCA	117	−125		−67/0.493	−12/+65.6	12/−52.7	29/−51.6
CPBA	118	−111		−55/0.288	−2.8/+61.2		31/−64.8
CPNA	188		3/+73.6		22/−20.0	36/+30.0	45/−77.1
CPPA		−65		−34/0.357			
PYBF	233			−73/0.366			
PYTFA	125	−118		−90/0.368			
PYCA			9/+105.2				32/−110.9
PYBA	163	−118		−63/0.423	−11/+15.3		7/−4.8
PYNA	168	−138		−76/0.452	−22/+19.2		8/−13.7
PYPA	249	−74		−46/0.386			

^{a} ΔC_p is the heat capacity change during the glass transition. ^{b} T_1 and T_2 are the onset temperature of the first (Phase I) and the second phase (Phase II) transition before fusion, respectively; + and − represent exothermic and endothermic, respectively.
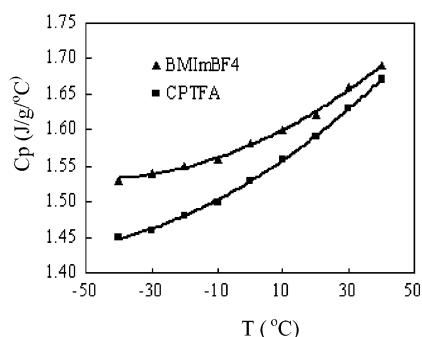
Figure 4. Heat capacities of CPTFA and BMImBF$_4$ relative to temperature.

BMImBF$_4$ and anions have a more apparent effect on heat capacity than cations. It can also be seen that the lactam ILs have slightly larger sensible heat storage densities than that of BMImBF$_4$, but they all are much higher than that of the heat transfer fluid (minimum 1.9 MJ/m^3) specified by the American National Renewable Energy Laboratory,[24] indicating these lactam-based ILs could potentially be used as excellent heat transfer fluids. The temperature dependency of the heat capacities for BMImBF$_4$ and CPTFA over the temperature range of −40 to 40 °C was also conducted, and the results suggested that the heat capacity of BMImBF$_4$ is higher than that of CPTFA below 50 °C and may be lower than that of CPTFA above 50 °C. In addition, the heat capacity of CPTFA has a relatively strong temperature dependency that is fitted to the following quadratic eq 3

$$C_p = -1.145 \times 10^{-4} T^2 + 5.584 \times 10^{-3} T + 1.590 \quad (3)$$

Thermal Decomposition Temperature. The decomposition temperatures (T_d) from the TG-DTA results (Table 4) show that the thermal stability of the lactam-based ILs is in the temperature range of 117−249 °C, depending on the structure of the cations and anions. With the same anions, the ILs containing the caprolactam cation have slightly higher thermal stability than the ILs containing the pyrrolidonium cation. In comparison to cations, anions have a stronger impact on the thermal stability of the lactam-based ILs. Typical TG/DTA results of CPTFA and CPBF are shown in Figure 5.

Phase Behavior. The phase behavior of the lactam-based ILs, such as freezing, melting, and glass transition, were studied with DSC. The results are summarized in Table 4. During cooling from 110 to −150 °C at 10 °C/min, a heat capacity change corresponding to the glass transition is observed for most of the lactam-based ILs, whereas the freezing process is observed only for CPNA and PYCA with a freezing point of 3 and 9 °C corresponding to a freezing enthalpy (ΔH_f) of +73.6 and +105.2 J/g, respectively. This means that the crystallization rates of all of the ILs except for CPNA and PYCA are very slow and that the supercooled liquids are fairly stable. An interesting phenomenon of supercooled liquid crystalline was also observed for most of the lactam-based ILs, as shown in Table 4 with onset temperature (T_c) of this slight transition. However, the lactam-based ILs show more different and complicated phase behavior in the heating scans from −150 to 110 °C. Six ILs, including CPBF, CPTFA, CPPA, PYBF, PYTFA, and PYPA, behave glass transition only. It is worth noting that PYTFA, having the lowest viscosity, manifests the lowest glass transition temperature of −90 °C. Coincidently, CPNA and PYCA, which have a solidification process, show no glass transition. Five ILs, such as CPCA, CPBA, CPNA, PYBA, and PYNA, have one or two phase transitions accompanying apparent exothermy (+) or endothermy (−) before complete fusion. The complex polymorphism is illustrated by the DSC trace for CPNA and PYCA as shown in Figure 6. It is postulated that after passing
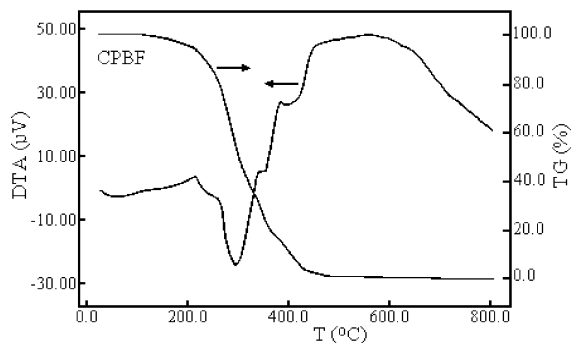
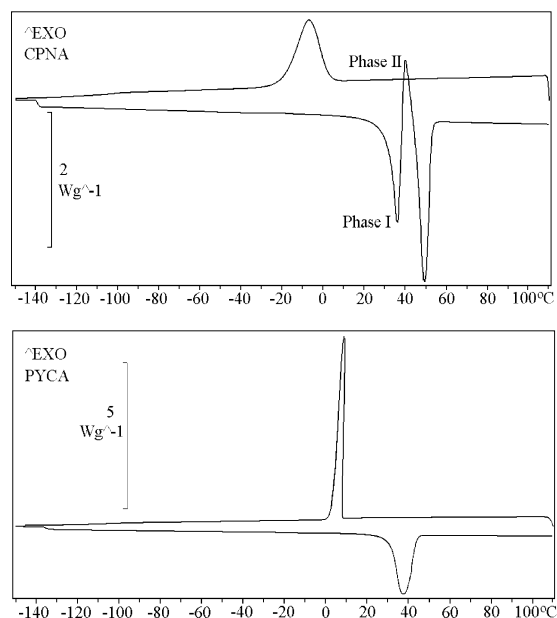**Figure 5.** TG-DTA trace for CPTFA and CPBF.

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Figure 6. DSC results for CPNA and PYCA.

through the glass transition temperature, the undercooling salts must crystallize and/or the cations and anions must reorganize to form a metastable crystal upon heating before complete fusion. Our analyses show a trend that has also been observed by Fox and co-workers.[25]

Conclusions

Several novel lactam-cation-based Brønsted acid ILs were prepared through a simple and atom-economic neutralization reaction between a lactam, such as caprolactam or butyrolactam, and a Brønsted acid. The density, viscosity, acidic scale, electrochemical window, conductivity, and phase behavior were measured and investigated in detail. In comparison to imidazolium ILs, lactam-cation-based Brønsted acidic ILs possess relatively less cost, lower toxicity, lower viscosity, comparable ionic conductivity, and a high enough thermal stability. These ILs could be produced easily in large amounts and have potentially wide applicable perspectives for fuel cell electrolytes, thermal transfer fluids, and acid-catalyzed reaction media and catalysts as replacements of conventional inorganic acids.

Supporting Information Available: Experimental instruments, general preparation procedures, and acidic scale measurement for the lactam-based ILs; ^{1}H-NMR, ^{13}C-NMR, and ESI-MS spectra of CPTFA. This material is available free of charge via the Internet at http://pubs.acs.org.

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