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SYNTHESIS OF DICATIONIC POLY(IONIC LIQUID)S WITH BRUSHED ARCHITECTURE AND THEIR HIGH THERMAL STABILITY

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ABSTRACT

Six branched chain dicationic poly(ionic liquid)s (DPILs) with an imidazolium cation on one side, an alkyl chain in the center, and a pyridinium cation on the other side are synthesized in this study. The thermal stability and solvent miscibility of these DPILs are also investigated. The results of this study show that the combined anions can greatly influence the solubility and thermal stability of these PILs. Among these polymers, dicationic poly(imidazolium-alkyl-pyridinium) bis(trifluoromethylsulfonyl)imide ionic liquids exhibit the highest thermal stability (> 390 °C). This thermal property makes them prime candidates for further chemical experimentation, investigation and application.

Keywords: Dication; Poly(ionic liquid)s; Thermal stability; Di-hexafluorophosphate anion; Di-bis(trifluoromethylsulfonyl)imide anion; solubility.

1. INTRODUCTION

Ionic liquids (ILs) are generally defined as organic/inorganic salts. With a melting point lower than 100 °C, they are considered to have good chemical and electrochemical stability, low flammability, negligible vapor pressure, and ionic conductivity. ILs have attracted considerable attention to chemists, and their applications are found in an increasing number of technological fields, such as reaction solvents (catalysis and organic chemistry), extraction solvents (analytical chemistry), and electrolyte materials (energy and electrochemistry) due to their remarkable properties. ILs are now considered as designer liquids because their physical and chemical properties. ILs can be adjusted or tuned by controlling the nature and the functionality of the cations and anions (Sowmiah *et al*. 2009; Welton 1999; Wang *et al*. 2017).

Poly(ionic liquid)s, namely, (PILs), are a new type of IL. They contain a polymerizable group in the IL monomer, and they are formed by some initiators (Washiro *et al*. 2004). PILs have recently been studied in various applications, such as Li-battery electrolytes (Ogihara *et al*. 2006), stationary phases in gas chromatography (Hsieh *et al*. 2007), and solid-phase microextraction (Young *et al*. 2016; Devasurendra *et al*. 2017). In other studies, the PILs are found to have high thermal stability. Kuei group reports that a good PIL gas chromatography (GC) stationary phase coated in capillary fused with silica tubing can separate many compounds with similar polarities, such as *m*-, *p*-, and *o*-xylenes, at the high temperature of 310 °C (Hsieh *et al*. 2007). In the SPME application for PIL modified electrodes, the high extraction efficiency of PIL is also related to its high thermal stability (Anderson *et al*. 2005). However, the PILs in the above applications are in the monocationic systems, and the thermal stability of these monocationic PILs is lower than 330 °C (Young *et al*. 2016; Devasurendra *et al*. 2017).

To improve the thermal stability of monocationic PILs, another type of IL, namely, dicationic ILs, which have two monocations, are combined into a dication (Anderson *et al*. 2005; Payagala *et al*. 2007; Chang *et al*. 2010; Chang *et al*. 2011). The tunability of dicationic ILs is enhanced by cationic moieties. Dicationic ILs are suitable in the applications of dye-sensitized solar cells (Zefer *et al*. 2009), organic synthesis (Han *et al*. 2005), and lubricants (Jin *et al*. 2006; Zeng *et al*. 2008). These ILs are further classified as geminal (the same two monocations that form the dication) or unsymmetrical (different monocations that form the dication). Each dication is associated with two identical or unsymmetrical anions, which can be either hydrophobic or hydrophilic.

Most dication ILs are composed of an unsymmetrically substituted nitrogen-containing monocation, such as imidazolium or pyridinium. This monocation will also has an inorganic anion of Cl-, Br-, PF_6-, BF_4-, or NTf_2- (bis(trifluoromethanesulfonyl)amide). However, to the best of our knowledge, no similar studies have been conducted in the polymeric systems. By incorporating polymeric moieties into a dicationic system, a new series of dicationic PILs (DPILs) is synthesized in this study. Their thermal decomposition temperature and their solubility in organic solvents will also be discussed.

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2. MATERIALS AND METHODS

2.1 Chemicals

The following chemicals are purchased from a commercial supplier, and they are used in this study without any pre-treatment: 1,3-dibromopropane (Alfa Aesar, purity: 99.9%), 1,4-dibromobutane (Alfa Aesar, purity: 99.9%), Pyridine (Fluka, purity: 98%), 1-vinylimidazole (Fluka, purity: 99.9%), 2,2-azobis-isobutyronitrile (AIBN) (Showa, purity: 99.9%), potassium hexafluorophosphate (KPF_6) (Aldrich, purity: 99.9%), lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) (Aldrich, purity: 99.9%), and propanol (J.T. Baker, ACS grade, ≤ 0.01% H_2O).

2.2 Measurement

The ^{1}H spectra (Figure S1a-S1h) of the purified products were recorded in D_2O (Cambridge Isotope Laboratories Inc., 99.9% D) or DMSO-d_6 (Cambridge Isotope Laboratories Inc., 99.9% D), using a Bruker Avance 200 spectrometer at 200 MHz in ^{1}H (compounds **1a-1b**) or a Bruker Avance 500 spectrometer at 500 MHz in ^{1}H and at 125 MHz in ^{13}C (compounds **2a-2b**, **3a-3b**, **4a1-4a2**, and **4b1-4b2** only in ^{1}H). Elemental analyses were conducted using an Elementar analyzer (model: Vario EL III). The relative molecular weights of these DPILs were measured by a UV detector and a gel permeation chromatography (GPC) device, equipped with a Jasco-980PU pump, Waters Styragel HR4E (Mw: 50-100,000). Thermogravimetric analysis (TGA, model: TGA-50, Shimadzu) was conducted at a heating rate of 5 °C min^{-1} (T*d* is the temperature corresponding to 10% weight loss). The solubility of the ILs was tested using common organic solvents.

2.3 General procedure for the synthesis of dicationic PILs

The general procedure for the synthesis of dicationic PILs (DPILs) is shown in Scheme 1. Compounds **1a** and **1b** are prepared by stirring pyridine (1.0 mmole), 1,3-dibromopropane and 1,4-dibromobutane (1.5 mmole) at the room temperature for 4 days, respectively. The mixture is then washed with ethyl acetate to remove any unreacting reactants, followed by the filtration to obtain white precipitates of **1a** and **1b**. Compounds **2a** and **2b** are prepared by performing a substitution reaction for compounds **1a** and **1b** with 1-vinylimidazole (2.0 mmole) in methanol at 60 °C refluxed for 2 days, respectively. The products are precipitated with ethyl acetate. Compounds **3a** and **3b** are prepared by reacting compound **2a** (for **3a**) and **2b** (for **3b**) with AIBN (5 mole %) in a co-solvent (EtOH/$CHCl_3$, volume ratio EtOH: $CHCl_3$ = 1:1) at 80 °C refluxed for 24 hours. The products are precipitated with ethyl acetate. Compounds **4a1-4a2** and **4b1-4b2** are prepared respectively by proceeding anion exchange for compound 3a and 3b with 1.5 mmol KPF_6 (compounds **4a1** and **4b1**) and $LiNTf_2$ (compound **4a2** and **4b2**) in deionized water at the room temperature for 3 days. The precipitates are filtrated to afford the corresponding salts.

2.3.1. *[1-(3-bromopropyl)pyridinium] bromide* (***1a***) Yield 99%. ^{1}H-NMR (200MHz, D_2O): δ 2.58 (quin, *J* = 6.4Hz, 2H), 3.48 (t, *J* = 6.4Hz, 2H), 4.77-4.82 (m, 2H), 8.08 (t, *J* = 6.8Hz, 2H), 8.54 (t, *J* = 6.8Hz, 1H), 8.89 (d, *J* = 6.8Hz, 2H).

2.3.2. *[1-(4-bromobutyl)pyridinium] bromide* (***1b***) Yield 99%. 1H-NMR (200MHz, D_2O): δ 1.81 (quin, J = 6.4Hz, 2H), 2.04 (quin, *J* = 6.4Hz, 2H), 3.41 (t, *J* = 6.4Hz, 2H), 4.55 (t, *J* = 6.4Hz, 2H), 7.97 (t, *J* = 6.8Hz, 2H), 8.44 (t, *J* = 6.8Hz, 1H), 8.76 (d, *J* = 6.8Hz, 2H).

2.3.3. *[1-(1-pyridinium-yl-propyl)-3-vinylimidazolium] dibromide* (***2a***) Yield 85%. ^{1}H-NMR (500MHz, DMSO-d_6): δ 2.72 (quin, *J* = 7.1Hz, 2H), 4.48 (t, *J* = 7.1Hz, 2H), 4.90 (t, *J* = 7.1Hz, 2H), 5.48 (dd, J = 8.8, 2.2Hz, 1H), 6.10 (dd, J = 15.6, 2.2Hz, 1H), 7.43 (dd, *J* = 15.6, 8.8Hz, 1H), 8.15 (s, 1H), 8.26 (t, *J* = 7.1Hz, 1H), 8.40 (s, 1H), 8.72
(t, *J* = 7.4Hz, 1H), 9.36 (d, *J* = 6.6Hz, 2H), 9.93 (s, 1H). ^{13}C-NMR (125MHz, DMSO-d6): δ 30.4, 46.1, 57.4, 108.9, 119.3, 123.2, 128.2, 128.8, 135.6, 144.9, 145.8.

2.3.4. *[1-(1-pyridinium-yl-butyl)-3-vinylimidazolium] dibromide* (***2b***) Yield 80%. ^{1}H-NMR (500MHz, DMSO-d_6): δ 1.91-2.09 (m, 4H), 4.35-4.39 (m, 2H), 4.35-4.47 (m, 2H), 4.79-4.89 (m, 2H), 5.45 (dd, *J* = 8.8, 2.2Hz, 1H), 6.08 (dd, *J* = 15.7, 2.2Hz, 1H), 7.40 (dd, *J* = 15.7, 8.8Hz, 1H), 8.09 (s, 1H), 8.23 (t, *J* = 6.7Hz, 2H), 8.36 (s, 1H), 8.69 (t, *J* = 7.3Hz, 1H), 9.31 (t, *J* = 6.2Hz, 2H), 9.88 (s, 1H). ^{13}C-NMR (125MHz, DMSO-d_6): δ 25.6, 27.3, 48.3, 59.6, 108.8, 119.2, 123.2, 128.1, 128.8, 135.4, 144.8, 145.6.

2.3.5. *poly[1-(1-pyridinium-yl-propyl)-3-sec-butylimidazolium] dibromide* (***3a***) Yield 75%. The ^{1}H NMR spectrum is shown in Figure S1c. Elem. Anal. Calcd. For $(C_{13}H_{17}Br_2N_3)m \cdot 2H_2O$: C, 37.98; H, 5.15; N, 10.22%. Found: C, 38.28; H, 5.48; N, 10.36%. Relative molecular weight: 43,400 g mol^{-1}.

2.3.6. *poly[1-(1-pyridinium-yl-butyl)-3-sec-butylimidazolium] dibromide* (***3b***) Yield 70%. The ^{1}H NMR spectrum is shown in Figure S1d. Elem. Anal. Calcd. For $(C_{14}H_{19}Br_2N_3)m \cdot 1H_2O$: C, 41.30; H, 5.20; N, 10.32%. Found: C, 40.67; H, 5.52; N, 10.23%. Relative molecular weight: 45,700 g mol^{-1}.

2.3.7 *poly[1-(1-pyridinium-yl-propyl)-3-sec-butylimidazolium] dihexafluorophosphate* (***4a1***) Yield 88%. The ^{1}H NMR spectrum is shown in Figure S1e. Elem. Anal. Calcd. For $(C_{13}H_{17}F_{12}N_3P_2)m$: C, 30.91; H, 3.39; N, 8.32%. Found: C, 30.63; H, 3.51; N, 8.19%. Relative molecular weight: 57,100 g mol^{-1}.

2.3.8. *poly[1-(1-pyridinium-yl-butyl)-3-sec-butylimidazolium] dibis(trifluoromethylsulfonyl)imide* (***4a2***) Yield 83%. The ^{1}H NMR spectrum is shown in Figure S1f. Elem. Anal. Calcd. For $(C_{17}H_{17}N_5F_{12}O_8S_4)m$: C, 26.33; H, 2.21; N, 9.03%. Found: C, 26.49; H, 2.56; N, 9.17%. Relative molecular weight: 64,400 g mol^{-1}.

2.3.9. *poly[1-(1-pyridinium-yl-butyl)-3-sec-butylimidazolium] dihexafluorophosphate* (***4b1***) Yield 84%. The ^{1}H NMR spectrum is shown in Figure S1g. Elem. Anal. Calcd. For $(C_{14}H_{19}F_{12}N_3P_2)m$: C, 32.38; H, 3.69; N, 8.09%. Found: C, 32.31; H, 3.80; N, 8.08%. Relative molecular weight: 54,100 g mol^{-1}.

2.3.10. *poly[1-(1-pyridinium-yl-butyl)-3-sec-butylimidazolium] dibis(trifluoromethylsulfonyl)imide* (***4b2***) Yield 81%. The ^{1}H NMR spectrum is shown in Figure S1h. Elem. Anal. Calcd. For $(C_{18}H_{19}N_5F_{12}O_8S_4)m$: C, 27.38; H, 2.43; N, 8.87%. Found: C, 27.71; H, 2.86; N, 9.09%. Relative molecular weight: 62,300 g mol^{-1}.

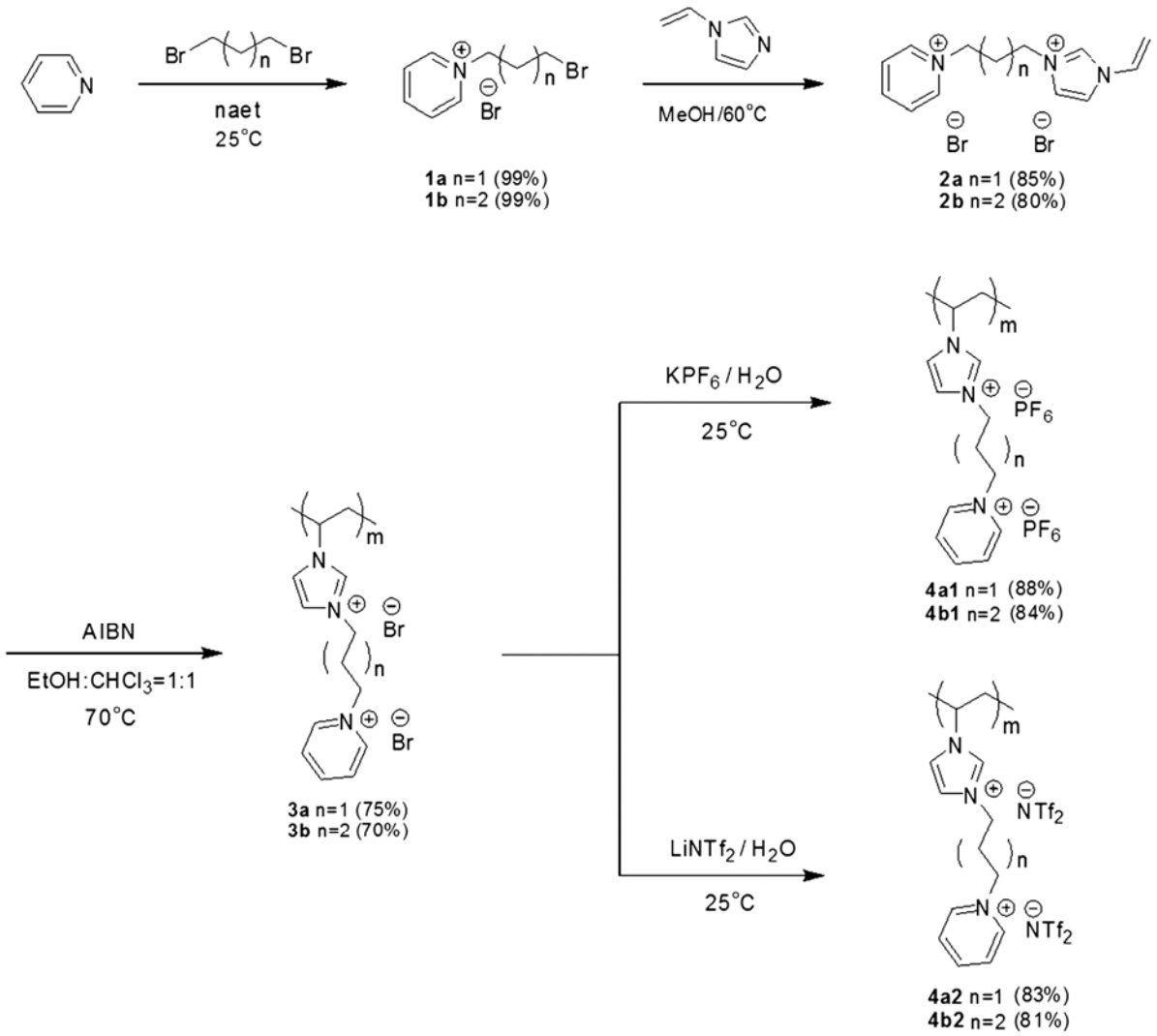
3. RESULTS AND DISCUSSION

3.1 Synthesis of DPILs containing di-PF6 and di-NTf2 anions

The synthesis procedure, chemical structures, and product yields are summarized in Scheme 1. Target DPILs, **3a-3b**, **4a1-4a2**, and **4b1-4b2**, are prepared according to the procedures in the previous research (Anderson *et al*. 2005; Payagala *et al*. 2007; Mecerreyes 2011). First, pyridine is used rather than strong nucleophiles, such as 1-methylimidazole, to react with 1,3-dibromopropane and 1,4-dibromobutane, respectively. Pyridine was used because it will only replace one bromine of 1,3-dibromopropane or 1,4-dibromobutane. When using stronger nucleophiles, both bromines will be replaced. Second, 1-vinylimidazole is used to conduct the S_N2 substitution reaction to synthesize the ionic liquid monomers. Third, the radical initiator, AIBN, is used to perform radical polymerization to form the new brush-type DPILs (**3a** and **3b**). Finally, the Br- ion in the product of the third step will have anion exchanges with inorganic salts (KPF_6 for **4a1** and **4b1**, LiNTf2 for **4a2** and **4b2**). In the present study, the DPILs are found to have unsymmetrical dication and each polymeric dication is associated with two identical anions. The linkage chain system is a propyl chain in compounds **3a**, **4a1**, and **4a2**. A butyl chain is found in **3b**, **4b1**, and **4b2**.

Figure 1a and 1b show the ^{1}H spectra of monomers and the polymerized form. **2a** and **2b** are spectra A and E. **3a** and **3b** are spectra B and F. **4a1** and **4a2** are spectra C and D. **4b1** and **4b2** are spectra G and H, respectively. A disappearance of the vinyl signals is observed (for example in **2a**) at 5.50, 5.87, and 7.20 ppm, along with the appearance of new signals of the protons of the polymeric backbone (for example in **3a**) at 4.70 and 2.75 ppm. The polymers exhibit a broadening of the signals, corresponding to the classical spectrum.

1-vinylimidazole can be used to synthesize monomers that can easily be reserved in the room temperature. Previous studies (Washiro *et al*. 2004; Ogihara *et al*. 2006) reported that monomers containing an acrylic or styrene functional group are not easily reserved in the room temperature. This is because the acrylic or styrene functional group can perform anion polymerization and form some oligomers in the room temperature when halide anions exist in the environment.



Scheme 1 Synthesis procedures for DPILs.

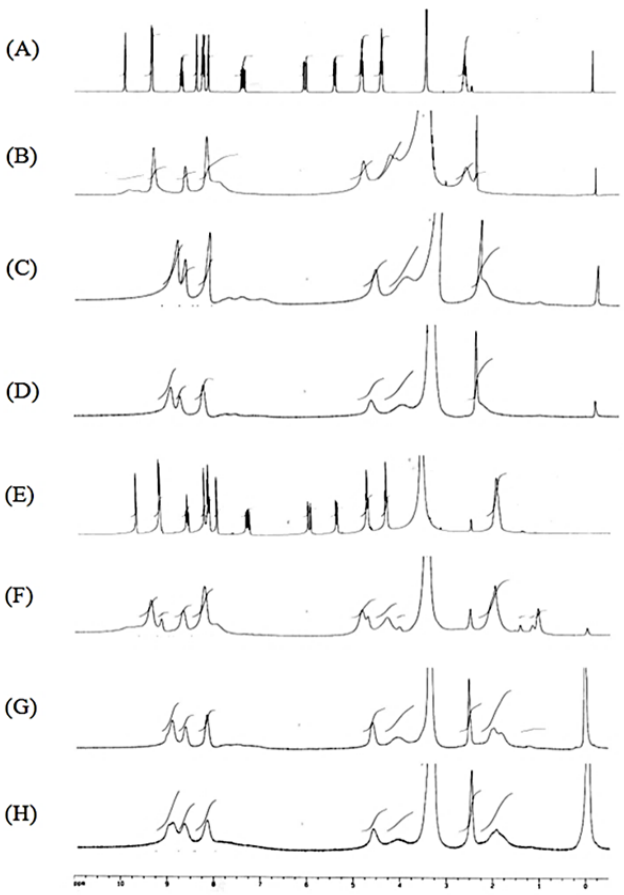


Fig. 1 1H NMR spectra of monomers (2a and 2b) and polymerized form compounds (3a-3b, 4a1-4a2, and 4b1-4b2): propyl chain compounds (A: 2a, B: 3a, C: 4a1, D: 4a2) and butyl chain compounds (E: 2b, F: 3b, G: 4b1, H: 4b2).

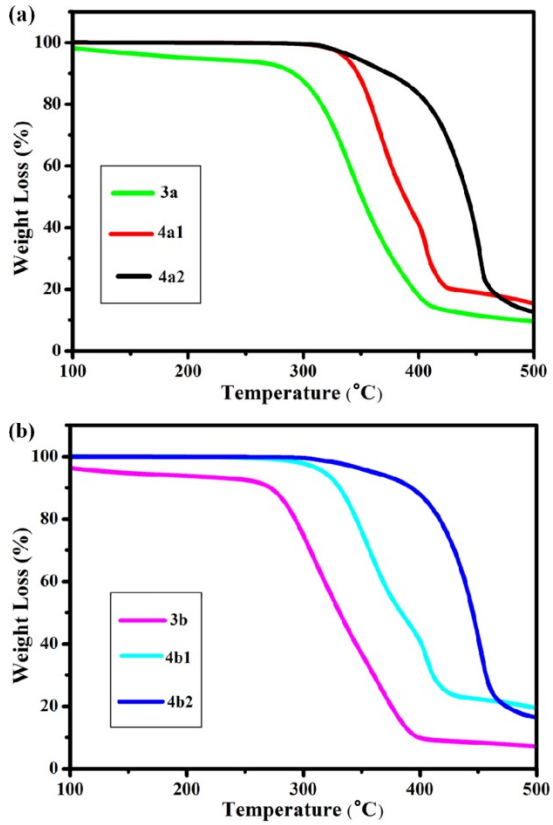


Fig. 2 TGA curves for dicationic polymeric ionic liquids obtained at a heating rate of 5 °C min^{-1} for (a) propyl chain compounds (3a, 4a1, and 4a2), (b) butyl chain (3b, 4b1, and 4b2).

3.2 Thermal stability

As shown by the TGA curves in Figure 2a and 2b, the dicationic polymeric ILs (DPILs) exhibit good thermal stability, ranging from 270 ~ 400 °C. According to the data summarized in Table 1, DPILs containing di-bis(trifluoromethylsulfonyl)imide (di-NTf_2) anions are thermally more stable than those containing di-bromide (di-Br) or di-hexafluorophosphate (di-PF_6) anions (**4a2** > **4a1** > **3a**; **4b2** > **4b1** > **3b**). This finding is consistent with previous research results (Hsieh *et al*. 2007; Anderson *et al*. 2005; Payagala *et al*. 2007; Chang *et al*. 2010 and 2011; Hsieh *et al*. 2008; Ngo *et al*. 2000; Awad *et al*. 2004; Kroon *et al*. 2007). Moreover, Stevens group (Maton *et al*. 2013) indicates that ILs containing NTf anions have high thermal stability because the anions require a high decomposition activation energy to decompose to SO at the elevated temperature. In this study, compounds **4a2** and **4b2** have the highest thermal stability among the synthesized DPILs, and they are also thermally more stable than mono-cationic PILs containing mono-NTf_2 anions.

The nucleophilicity of the bromide anion is found to play an important role in the thermal stability of ILs (Hsieh *et al*. 2008; Ngo *et al*. 2000; Awad *et al*. 2004; Kroon *et al*. 2007). That is, it decreases the thermal stability of ILs when the temperature is increased (**3a** and **3b**). It is noted that the thermal stability of compounds **3a** and **3b** does not significantly differ from other PILs containing mono-Br anions shown in Table 1. It can be rationalized that **3a** and **3b** have di-Br anions, which give the compounds higher nucleophilicity than those of PILs with mono-Br anions. This study also proves that the thermal stability of dicationic ILs can be higher than those of monocationic systems without di-Br anions.

Table 1 Comparison of Td values between DPILs and monocationic polymeric ILs.

Polymers	T_d (°C) [a]	T_d (°C) [b]	References
3a	277	290	This work
3b	267	273	This work
4a1	331	355	This work
4a2	343	390	This work
4b1	336	353	This work
4b2	365	410	This work
PVBIm$^+$Br$^-$	255	275	Mecerreyes, D. 2011
PVBIm$^+$PF$_6^-$	287	301	Mecerreyes, D. 2011
PVBIm$^+$NTf$_2^-$	324	350	Mecerreyes, D. 2011
PVOIm$^+$Br$^-$	265	280	Hsieh, Y.N. *et al*. 2008
PVOIm$^+$PF$_6^-$	280	295	Hsieh, Y.N. *et al*. 2008
PVOIm$^+$NTf$_2^-$	360	380	Hsieh, Y.N. *et al*. 2008
PVHexIm$^+$NTf$_2^-$	330	375	Hsieh, Y.N. *et al*. 2007

[a] T_d onset.
[b] T_d at 10% weight loss.
[c] PVBIm: poly(1-vinyl-3-butylimidazolium).
[d] PVOIm: poly(1-vinyl-3-octylimidazolium).
[e] PVHexIm: poly(1-vinyl-3-hexylimidazolium).

3.3 Solubility

The solubility behavior of the synthesized DPILs in several selected solvents is summarized in Table 2. In this study, "soluble" is defined that 5 mg of the DPIL can be completely dissolved in 1 mL of the solvent in the room temperature. Previous studies (Anderson *et al*. 2005; Payagala *et al*. 2007) indicates that the solubility behavior of geminal dicationic ILs is quite similar to that of monocationic ionic liquids; namely, PF_6- and NTf_2-salts are immiscible with water, MeOH, and EtOH whereas Br-salts are miscible with these solvents. PF6- and NTf_2- salts are generally soluble in acetone, tetrahydrofuran (THF), and EtOAc.

However, Table 2 indicates that the synthesized DPILs containing di-Br anions are soluble in water and MeOH, but not soluble in EtOH (polymers **3a** and **3b**). DPILs based on di-PF_6 or di-NTf_2 anions are miscible with acetone and EtOAc, but they must be heated. DPILs with di-PF_6 or di-NTf_2 anions can also become soluble in MeOH when heated, but they are not soluble in THF and Et_2O. Some DPILs exhibit solubility behavior similar to monocationic PILs containing Br-, PF_6-, or NTf_2- as previous research has indicated (Marcilla *et al*. 2004). In the current study, the existence of the anion structure is found to influence the solubility of the polymer. This finding may be attributed to the higher ionic strength in DPIL polymers.

4. CONCLUSION

Dicationic PILs that contain di-Br, di-PF_6, or di-NTf_2 anions are synthesized in this study. The DPILs exhibit significantly better thermal stability than the PILs. The DPILs based on di-Br anions are miscible with water and MeOH. The DPILs containing di-PF_6 or di-NTf_2 anions are soluble in acetone and EtOAc when they are heated. The current research results suggest that both the anions and the higher ionic strength of DPILs will have influence on the polarity and the thermal stability of the DPILs. The DPILs containing NTf_2 reveal a very high thermal stability (~ 410 °C), that makes them suitable for more chemical experiments and applications.

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Competing Interests

The authors declare no competing interests.

Supporting information available:

The ^{1}H NMR spectra of the monomers (**2a** and **2b**) and polymerized form compounds (**3a-3b**, **4a1-4a2**, and **4b1-4b2**) are shown in Figure S1a-S1h.

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Table 2 Comparison of solubility in various organic solvents between DPILs synthesized in this study

Polymers	DMSO	H_2O	MeOH	EtOH	Et_2O	THF	EtOAc	Acetone
3a	+	+	+	−	−	−	−	−
3b	+	+	+	−	−	−	−	−
4a1	+	−	±	−	−	−	±	±
4a2	+	−	±	−	−	−	±	±
4b1	+	−	±	−	−	−	+	±
4b2	+	−	±	−	−	−	+	±

+: Miscible
±: soluble on heating
−: immiscible
testing temperature: 25 ± 1 °C

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