

Synthesis and characterization of branched polymeric ionic liquids with imidazolium chloride segments

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Abstract A branched polymeric ionic liquid (PIL) with imidazolium cation segments in the main chain connecting branching points was prepared in 95% yield by heating an equimolar mixture of 1,3,5-tris-(4-chlorobutoxy)-benzene and 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene at 80 °C for 16 h. Similarly, condensation of a mixture of 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene and 1,4-dichlorobutane in 1:1.5 molar ratio produced a second branched PIL in 94% yield. These branched PILs were characterized by FT-IR, ^1H , ^{13}C NMR, TGA, and elemental analysis.

Keywords Polymeric ionic liquid · Imidazolium cation · Branched polymer

Introduction

Polymeric ionic liquids (PILs) which can combine ionic liquid and polymer properties into a single material have stimulated interest in a number of fields in recent years. The swift progress and explosive growth in this area is reflected by the large body of recent publications. New developments in PILs are reviewed in three recent reviews [1–3], and imidazolium-based PILs are discussed in two other recent reviews [4, 5] justifying the importance of PILs. PILs have the advantage over traditional ionic liquids in new ionic liquid applications which require properties like improved processability and mechanical stability, and this new generation of smart polymers has already found applications in a vast array of fields. Some of the most notable PIL applications are in, lithium-polymer batteries [6], dye-sensitized solar cells [7], gene-delivery vectors [8], gas separation membranes [9], conducting polymer coatings [10], electrospinnable polymers [11] electric field actuators [12],

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GC stationary phases [13], anion detectors [14], and proton conducting polymers [15].

Imidazolium group containing PILs are a major sub group in this type of polymers and has caught the special attention due to gas absorption properties of the imidazolium cation, particularly towards carbon dioxide and water vapor. Gin and Noble recently reported [16] the preparation of a PIL membrane using an imidazolium ionene with the bromide counterion, which showed good H_2/CO_2 selectivity. Additionally, they found that a similar membrane with Tf_2N anion in place of the bromide can exhibit good CO_2/CH_4 and CO_2/N_2 selectivities. In another recent communication on imidazolium PILs, Schubert et al. reported the synthesis of 4,4-imidazolium ionenes under microwave irradiation, and their application of these PILs with Cl or Br counterions as humidity absorbers [17]. Furthermore, synthesis of imidazolium group containing linear ionene polyesters [18] and block copolymers [19] are also known.

Our interests in the use of ionic liquids in biomass processing [20–22] and thermal properties of imidazolium ionic liquids [23] have led us to explore possible synthetic methods for the preparation of PILs with ionic liquid structure in the main polymer chain, rather than as a pendant group. We recently reported [24] the synthesis of poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) by two alternative approaches, and characterization using spectroscopic methods. As an expansion of this novel approach towards imidazolium PIL synthesis, we have prepared the first examples of branched PILs with imidazolium cation segments in the main chain connecting branching points. In this communication we report the synthesis, and characterization of two branched imidazolium polymers, opening a new sub group of PILs with a new PIL architecture.

Experimental

Materials and physical measurements

Imidazole, 1,4-dichlorobutane, 1-bromo-4-chlorobutane, and 1,3,5-trihydroxybenzene were purchased from Aldrich Chemical Co. ^1H NMR Spectra were recorded in CDCl_3 or in $\text{DMSO}-d_6$ on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ^{13}C NMR were recorded in the same spectrometer operating at 100 MHz; chemical shifts were measured relative to CDCl_3 or $(\text{CD}_3)_2\text{SO}$ and converted to $\delta(\text{TMS})$ using $\delta(\text{CDCl}_3) = 77.16$, and $\delta(\text{CD}_3)_2\text{SO} = 39.52$. FT-IR spectra were recorded on a JASCO-470 PLUS IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out in air on a TA instruments TGA 2050 system with scan rate of $10^\circ\text{C}/\text{min}$. Elemental analysis was performed at QTI laboratories, New Jersey.

Synthesis of 1,3,5-tris-(4-chlorobutoxy)-benzene (**2**)

A mixture of 1,3,5-trihydroxybenzene (1.26 g, 10 mmol) and sodium hydroxide (1.20 g, 30 mmol) in 20 mL of dimethylsulfoxide was prepared. Then, this mixture

was slowly added to a solution of 1-bromo-4-chlorobutane (5.15 g, 30 mmol) in 10 mL of dimethylsulfoxide. The resulting solution was stirred for 2 days at room temperature. The mixture was poured into 100 mL of water, and then extracted with methylene chloride (5×20 mL), combined organic layer was dried (anhydrous Na_2SO_4), and concentrated to give 1,3,5-tris-(4-chlorobutoxy)-benzene (**2**) as a pale yellow viscous oil, 3.55 g, 89% yield. Found: C, 54.08; H, 6.98%. Calc. for $\text{C}_{18}\text{H}_{27}\text{Cl}_3\text{O}_3$: C, 54.35; H, 6.84%. ^1H NMR (CDCl_3) δ 1.93 (m, 12H), 3.59 (t, 6H, $J = 6.0$ Hz), 3.93 (t, 6H, $J = 6.0$ Hz), 6.04 (s, 3H). ^{13}C NMR (CDCl_3) δ 26.6, 29.3, 44.7, 66.9, 93.9, 160.7.

Synthesis of 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**)

A mixture of imidazole (0.613 g, 9.0 mmol) and sodium hydroxide (0.36 g, 9.0 mmol) in 10 mL of dimethylsulfoxide was stirred at 70 °C for 1 h, and cooled to room temperature. Then a solution of 1,3,5-tris-(4-chlorobutoxy)-benzene (**2**) (1.193 g, 3.0 mmol) in 10 mL of dimethylsulfoxide was added slowly, and stirred at room temperature for 1 day. The resulting mixture was poured into 100 mL of water and extracted with methylene chloride (5×20 mL), combined organic layer was dried (anhydrous Na_2SO_4), and concentrated to give 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**) as a pale yellow viscous oil, 1.30 g, 88% yield. Found: C, 65.55; H, 7.58; N, 17.23%. Calc. for $\text{C}_{27}\text{H}_{36}\text{N}_6\text{O}_3$: C, 65.83; H, 7.37; N, 17.06%. ^1H NMR (CDCl_3) δ 1.67 (m, 6H), 1.89 (m, 6H), 3.84 (t, 6H, $J = 6.0$ Hz), 3.95 (t, 6H, $J = 6.0$ Hz), 5.94 (s, 3H), 6.88 (bs, 3H), 6.98 (bs, 3H), 7.48 (bs, 3H). ^{13}C NMR (CDCl_3) δ 26.3, 27.9, 46.7, 67.1, 93.8, 118.9, 129.1, 137.0, 160.6.

Synthesis of branched polymeric ionic liquid **4**

A mixture of 1,3,5-tris-(4-chlorobutoxy)-benzene (**2**) (0.214 g, 0.538 mmol) and 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**) (0.265 g, 0.538 mmol) was heated in a sealed tube, under a nitrogen atmosphere, at 80 °C, for 16 h using an oil bath. The product was allowed to cool to room temperature and washed with methylene chloride (5×3 mL), dried under vacuum at room temperature to give 0.455 g (95% yield) of branched PIL **4** as a light brown gummy solid. Found: C, 59.23; H, 7.41; N, 8.88%. Calc. for $\text{C}_{45}\text{H}_{63}\text{N}_6\text{O}_6\text{Cl}_3 \cdot 1.5 \text{H}_2\text{O}$: C, 58.92; H, 7.25; N, 9.16%. FT-IR: 640, 753, 821, 954, 1023, 1160, 1402, 1460, 1562, 1599, 2877, 2941, 3413 cm^{-1} . TGA: decomposition onset temperature 291 °C, DTG: peaks at 342 and 500 °C. ^1H NMR spectrum of **4** is shown in Fig. 3.

Synthesis of branched polymeric ionic liquid **5**

A mixture of 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**) (0.304 g, 0.618 mmol) and 1,4-dichlorobutane (0.118 g, 0.927 mmol) was heated in a sealed tube, under a nitrogen atmosphere, at 80 °C, for 16 h using an oil bath. The product was allowed to cool to room temperature and washed with methylene chloride (5×3 mL), dried under vacuum at room temperature to give branched PIL **5** as a light brown gummy solid, 0.417 g, 94% yield. Found: C, 55.40; H, 7.55; N, 11.48%. Calc. for

$C_{33}H_{48}N_6O_3Cl_3 \cdot 2H_2O$: C, 55.11; H, 7.29; N, 11.69%. FT-IR: 642, 758, 825, 954, 1025, 1163, 1406, 1465, 1564, 1603, 2874, 2952, 3428 cm^{-1} . TGA: decomposition onset temperature 240 $^{\circ}C$, DTG: peaks at 278, 310, and 500 $^{\circ}C$. 1H and ^{13}C NMR spectra of **5** are shown in Fig. 4.

Results and discussion

Synthesis and characterization of monomers

Monomers required for the preparation of branched PILs were first synthesized as shown in Fig. 1. Alkylation of 1,3,5-trihydroxybenzene (**1**) with three equivalents of 1-bromo-4-chlorobutane gave 1,3,5-tris-(4-chlorobutoxy)-benzene (**2**). 1H NMR spectrum of **2** showed two triplets at 3.59 and 3.93 ppm, corresponds to six protons each, and these peaks were assigned to $-CH_2-Cl$, and $-CH_2-O$ methylene groups of the three 4-chlorobutoxy groups attached to the benzene ring. ^{13}C NMR spectrum of **2** showed six peaks, further confirming the structure. The chloro ether **2** was then reacted with three equivalents of sodium salt of imidazole to produce 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**). 1H NMR spectrum of **3** showed two triplets at 3.84 and 3.95 ppm, corresponds to six protons each, and these peaks were assigned to $-CH_2-N$, and $-CH_2-O$ methylene groups of the three 4-imidazol-1-yl-butoxy groups attached to the benzene ring. Additionally, three broad peaks at 6.88 (3H), 6.98 (3H), and 7.48 (3H) ppm in the proton NMR were assigned to the three imidazole rings in the structure.

Synthesis and characterization of branched polymeric ionic liquids

Branched PIL 4

Alkylimidazolium type ionic liquids can be prepared by alkylation of the second nitrogen in *N*-substituted imidazoles [25], and this can be accomplished by conventional heating or microwave heating [26], with or without a solvent. Earlier we reported [24] the preparation of poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) via two different routes by exploiting this reaction. Here we have extended the same technique for the preparation of branched PILs. Heating an equimolar mixture of the monomers **2**, and **3** without a solvent, under a nitrogen atmosphere at 110 $^{\circ}C$

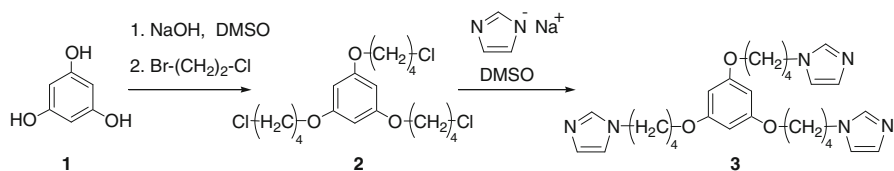


Fig. 1 Synthesis of branched PIL monomers; 1,3,5-tris-(4-chlorobutoxy)-benzene (**2**) and 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**)

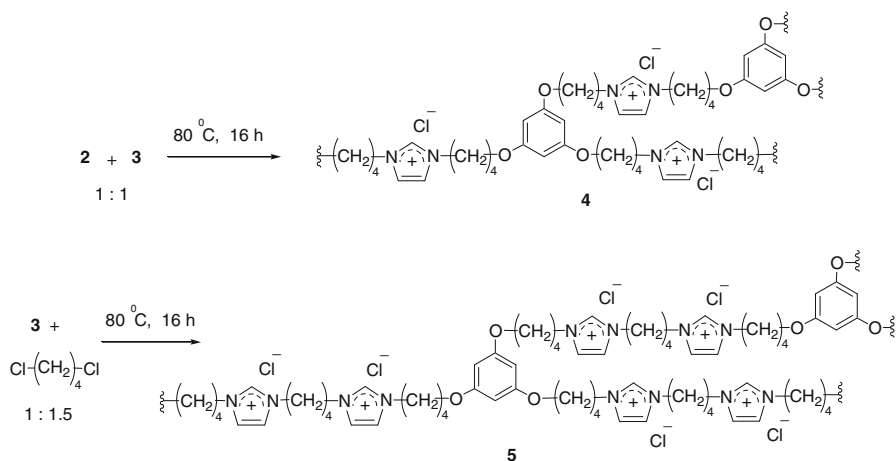


Fig. 2 Synthesis of branched PILs **4** and **5**

for 16 h produced the polymer **4**, (Fig. 2) which was purified by repeated washing with dichloromethane to remove unreacted monomer, and gave pure **4** as a brown gummy, hygroscopic solid in 95% yield. The new branched PIL is insoluble in water, unlike the linear imidazolium chloride polymer; poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) that we reported in the preceding publication [24], and in fact the branched polymer is practically insoluble in all the common organic solvents as well, and slightly soluble in warm DMSO and methanol. This solubility is just sufficient to record ^1H NMR, but was insufficient to record ^{13}C NMR spectrum. Furthermore, molecular weight determination was also not possible due to insolubility of **4**. The insoluble character can be attributed to the highly branched architecture of this polymer. FT-IR spectrum of **4**, recorded in a KBr pellet showed strong absorptions at 1562, 1460, and 1160 cm^{-1} characteristic of 1,3 dialkyl imidazolium cation, and these values are comparable to the IR absorptions in the linear imidazolium polymer, where the corresponding absorptions were 1565, 1463, and 1162 cm^{-1} , respectively [24]. The strong peak at 1023 cm^{-1} was assigned to C–O bonds, and the broad absorption at 3401 cm^{-1} is due to the absorbed water in the sample, showing the hygroscopic nature of the PIL. TGA of **4** showed decomposition onset temperature at $291\text{ }^\circ\text{C}$, which is comparable to the onset temperature of $300\text{ }^\circ\text{C}$, reported for the linear polymer [24]. Whereas, the derivative thermogravimetric curve showed two peaks at 342, and $500\text{ }^\circ\text{C}$, unlike the linear polymer of only one decomposition step.

^1H NMR of **4** recorded in $\text{DMSO}-d_6$ is shown in Fig. 3. It is interesting to note that C4 and C5 protons of the imidazolium ring appear as a single peak at 7.67 ppm showing the symmetry of the cation. The C2 proton in the imidazolium ring appears as a singlet at 9.20 ppm. These chemical shifts are comparable to the imidazolium ring proton chemical shifts of the previously reported linear imidazolium chloride polymer; poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) recorded in $\text{DMSO}-d_6$. The peak at 6.02 ppm was assigned to the aromatic ring hydrogens, whereas, the

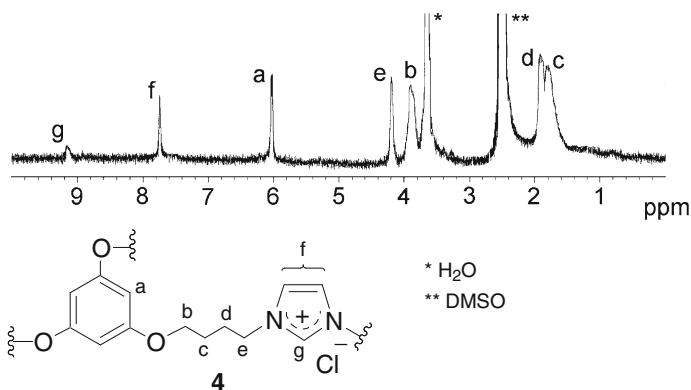


Fig. 3 ^1H NMR spectrum of **4** in $\text{DMSO-}d_6$

four methylene groups in the alkyl chain appeared as four broad peaks at 1.77, 1.89, 3.89, and 4.19 ppm. In an attempt to prepare polymer **4** by reacting a 1:1.5 mixture of **2** and sodium salt of imidazole gave a product with incomplete polymerization, with about 25% of unreacted $-\text{CH}_2-\text{Cl}$ groups, as evident in ^1H NMR spectrum of the sample.

Branched PIL **5**

The second branched PIL **5** was prepared by heating a 1:1.5 molar ratio mixture of **3** and 1,4-dichlorobutane under a nitrogen atmosphere at 110 °C for 16 h (Fig. 2). This material was also purified and characterized similar to **4**. The polymer **5** also showed an IR spectrum with peaks characteristic of the imidazolium cation. TGA of **5** gave somewhat lower decomposition onset temperature when compared to the polymer **4**. This polymer is also insoluble in water and common organic solvents, but slightly more soluble in $\text{DMSO-}d_6$ than **4**, just sufficient to record a weak ^{13}C NMR spectrum. This solubility difference may be due to the fact that branching points are relatively far apart in **5**, compared to the polymer **4**. ^1H and ^{13}C NMR spectra of branched PIL **5** recorded in $\text{DMSO-}d_6$, are shown in Fig. 4. Similar to the PIL **4**, C4 and C5 protons of the imidazolium ring in polymer **5** also appeared as a single broad peak at 7.85 ppm. The C2 proton in the imidazolium ring was assigned to the broad peak at 9.70 ppm, and relatively sharp peak at 6.06 was assigned to the aromatic ring. Additionally, broad peaks in the proton spectrum at 1.66, 1.93, 3.93, and 4.26 were assigned to methylene groups as shown in Fig. 4. In the ^{13}C spectrum, C4 and C5 carbons of the imidazolium ring appeared as a single peak at 122.9 ppm, and the peak at 136.9 was assigned to the C2, and these values are comparable to the imidazolium ring ^{13}C resonances seen in the linear polymer [24]. Additionally, peaks at 94.3 and 160.7 ppm can be allocated to the aryl ring, further supporting the proposed structure of branched PIL **5**.

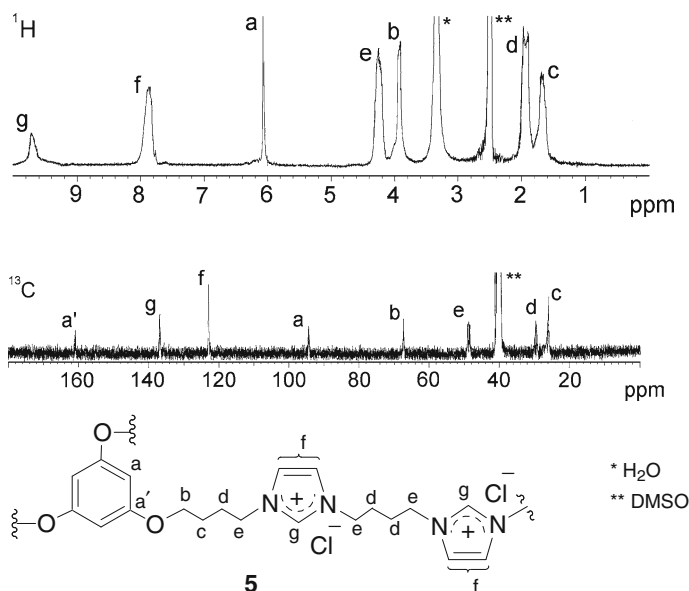


Fig. 4 ^1H and ^{13}C NMR spectra of **5** in $\text{DMSO-}d_6$

Conclusion

We have shown that branched PIL **4** can be prepared in excellent yield by condensation of an equimolar mixture of 1,3,5-tris-(4-chlorobutoxy)-benzene (**2**) and 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**). Similarly, condensation of a mixture of 1,3,5-tris-(4-imidazol-1-yl-butoxy)-benzene (**3**) and 1,4-dichlorobutane in 1:1.5 molar ratio produced the PIL **5**. As far as we are aware, these are the first examples of branched PILs with imidazolium cation segments in the main chain connecting branching points.

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References

1. Yuan J, Antonietti M (2011) Poly(ionic liquid)s: polymers expanding classical property profiles. *Polymer* 52:1469–1482
2. Green O, Grubjesic S, Lee S, Firestone MA (2009) The design of polymeric ionic liquids for the preparation of functional materials. *Polym Rev* 49:339–360
3. Lu J, Yan F, Texter J (2009) Advanced applications of ionic liquids in polymer science. *Prog Polym Sci* 34:431–448
4. Anderson EB, Long TE (2010) Imidazole and imidazolium-containing polymers for biology and material science applications. *Polymer* 51:2447–2454
5. Green MD, Long TE (2009) Designing imidazole-based ionic liquids and ionic liquid monomers for emerging technologies. *Polym Rev* 49:291–314

6. Sato T, Marukane S, Narutomi T, Akao T (2007) High rate performance of a lithium polymer battery using a novel ionic liquid polymer composite. *J Power Sources* 164:390–396
7. Freitas FS, de Freitas JN, Ito BI, De Paoli MA, Nogueira AF (2009) Electrochemical and structural characterization of polymer gel electrolytes based on a PEO copolymer and an imidazolium-based ionic liquid for dye-sensitized solar cells. *ACS Appl Mater Interfaces* 1:2870–2877
8. Zhang Y, Chen X, Lan J, You J, Chen L (2009) Synthesis and biological applications of imidazolium-based polymerized ionic liquid as a gene delivery vector. *Chem Biol Drug Des* 74:282–288
9. Bara JE, Lessmann S, Gabriel CJ, Hatakeyama ES, Nobel RD, Gin DG (2007) Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes. *Ind Eng Chem Res* 46:5397–5404
10. Chen H, Choi J-H, Cruz DS, Winey KI, Elabd YA (2009) Polymerized ionic liquids: the effect of random copolymer composition on ion conduction. *Macromolecules* 42:4809–4816
11. Chen H, Elabd YA (2009) Polymerized ionic liquids: solution properties and electrospinning. *Macromolecules* 42:3368–3373
12. Ricks-Laskoski HL, Snow AW (2006) Synthesis and electric field actuation of an ionic liquid polymer. *J Am Chem Soc* 128:12402–12403
13. Hsieh Y-N, Ho W-Y, Horng RS, Huang P-C, Hsu C-Y, Huangand H-H, Kuei C-H (2007) Study of anion effects on separation phenomenon for the vinyltolyl imidazolium based ionic liquid polymer stationary phases in GC. *Chromatographia* 66:607–611
14. Hu X, Huang J, Zhang W, Li M, Tao C, Li G (2008) Photonic ionic liquids polymer for naked-eye detection of anions. *Adv Mater* 20:4074–4078
15. Erdemi H, Akbey U, Meyer WH (2010) Conductivity behavior and solid state NMR investigation of imidazolium-based polymeric ionic liquids. *Solid State Ionics* 181(35–36):1586–1595
16. Carlisle TK, Bara JE, Lafrate AL, Gin DL, Noble RD (2010) Main-chain imidazolium polymer membranes for CO₂ separations: an initial study of a new ionic liquid- inspired platform. *J Membrane Sci* 359(1–2):37–43
17. Erdmenger T, Perevyazko I, Vitz J, Pavlova G, Schubert US (2010) Microwave- assisted synthesis of imidazolium ionenes and their application as humidity absorbers. *J Mater Chem* 20:3583–3585
18. Lee M, Choi UH, Cruz DS-D, Mittal A, Winey KI, Colby RH, Gibson WH (2011) Imidazolium polyesters: structure–property relationships in thermal behavior, ionic conductivity, and morphology. *Adv Funct Mater* 21:708–717
19. Williams SR, Cruz DS-D, Winey KI, Long TE (2010) Ionene segmented block copolymers containing imidazolium cations: structure–property relationships as a function of hard segment content. *Polymer* 51:1252–1257
20. Amarasekara AS, Owereh OS (2009) Hydrolysis and decomposition of cellulose in Brönsted acidic ionic liquids under mild conditions. *Ind Eng Chem Res* 48:10152–10155
21. Amarasekara AS, Owereh OS (2009) Homogeneous phase synthesis of cellulose carbamate silica hybrid materials using 1-*n*-butyl-3-methylimidazolium chloride ionic liquid medium. *Carbohydr Polym* 78:635–638
22. Amarasekara AS, Owereh OS (2010) Synthesis of a sulfonic acid functionalized acidic ionic liquid modified silica catalyst and applications in the hydrolysis of cellulose. *Catal Commun* 11:1072–1075
23. Amarasekara AS, Owereh OS (2011) Thermal properties of sulfonic acid group functionalized Brönsted acid ionic liquids. *J Therm Anal Calorim* 103:1027–1030
24. Amarasekara AS, Shanbhag P (2011) Synthesis and characterization of polymeric ionic liquid poly(imidazolium chloride-1,3-diylbutane-1,4-diyl). *Polym Bull* 67:623–629
25. Wasserscheid P, Welton T (2008) Ionic liquids in synthesis. Wiley-VCH Verlag GmbH, Weinheim
26. Varma RS, Namboodiri VV (2001) Solvent-free preparation of ionic liquids using a household microwave oven. *Pure Appl Chem* 73:1309–1313