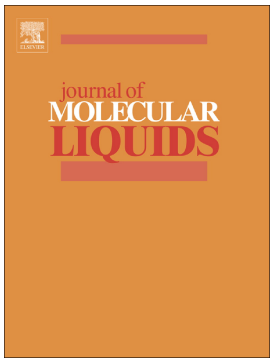

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Catalytic performance of a new Brønsted acidic oligo(ionic liquid) in efficient synthesis of pyrano[3,2-*c*]quinolines and pyrano[2,3-*d*]pyrimidines

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Abstract

An acidic liquid 1,3-ionene was synthesized from co-oligomerization of epichlorohydrin and imidazole followed by subjecting the resulting light oligomer to anion exchange with concentrated sulfuric acid and subsequent sulfonylation with chlorosulfonic acid. The ^{1}H- and ^{13}C NMR spectra of the synthesized oligo(ionic liquid) displayed significant chemical shifts on transferring the oligomer from D_2O to DMSO. This observation was interpreted as resulting from a conformational change in the multicationic oligomer. Application of this oligo(ionic liquid) as both solvent and acidic promoter to the synthesis of pyrano[3,2-*c*]quinolines and pyrano[2,3-*d*]pyrimidines gave fairly high yields of the products in short reaction times. The oligo(ionic liquid) is virtually stable, as could be stored for several months at room temperature and can be easily recycled several times in the synthesis of pyrano[3,2-*c*]quinolines and pyrano[2,3-*d*]pyrimidines at 80 °C without appreciable loss of activity.

Keywords: Oligo(ionic liquid); Ionene; pyrano[3,2-*c*]quinolines; pyrano[2,3-*d*]pyrimidines; Homogeneous catalysis; Conformational change.

1. Introduction

Recent decades have been witness to vast developments of ionic liquids (ILs) and so expansion of their applications from simple solvents to efficient catalysts [1], novel polymeric electrolytes [2], and surfactants [3]. Much of these advances have been made possible by modification of chemical and physical properties of ILs through variation of their cationic and anionic constituents. A much more diversity in physicochemical properties of ILs is achieved by fabricating them from functionalized [4-6] and multicationic [7] components. Multicationic ILs usually show a greater range of physical properties and self-assembling tendency than traditional mono-cationic ILs [8]. These diversity generating parameters provide flexibility for designing task-specific ILs and tuning their solubility as such to be easily recoverable from reaction mixtures by biphasic separation. Acidic ionic liquids are the elaborately functionalized ILs, which recently have attracted more interests due to their both solid acid and liquid acid advantages.

Synthesis of the first Brønsted acidic IL was reported [9] in 2002 and since then studies on these acidic liquids has grown up rapidly. Imidazolium-based ILs comprise one of the most studied classes of ILs. Selection of imidazolium ring as the cationic core of ILs is mainly due to its stability under oxidative and reductive conditions, low viscosity of imidazolium ILs and the ease with which it can be diversified [10]. The noncoordinative and ionic nature of imidazolium ILs make them privileged media for acid catalysis reactions [11]. In these ionic media, the protic groups gain increased ionic dissociation potential and the substrates serve as the sole proton acceptors. Among Brønsted-acidic ionic liquids, those bearing SO_3H and SO_4H groupings have received much attention because of their high acidity strength and catalytic efficacy [12].

Here, we describe the synthesis, spectroscopic structural elucidation, and valuable physical characteristics of a novel sulfuric acid-functionalized oligo(ionic liquid) (OIL). The synthesized OIL, which is structurally a liquid ionene sulfuric acid (ISA), was successfully evaluated as both solvent and acid promoter in the three-component probe synthesis of pyrano[3,2-*c*]quinolines and pyrano[2,3-*d*]pyrimidines. Synthesis of these compounds has long been the subject of numerous studies due to their diverse pharmacological activities [13,14]. Although several routes have, so far, been reported for synthesis of these compounds [15], they are commonly synthesized through three-component annulation of a pyran ring onto appropriate hydroxypyrimidones or hydroxyquinolones [16]. These reactions are not fisible by themselves, so many methods based on using a vareity of catalysts have been developed [17]. However, despite the obvious merit of the recent reported methods,

development of alternative green and efficient approaches are still in demand to avoid limitations such as use of expensive reagents, long reaction times, and laborious workup procedures.

2. Experimental Section

2.1 Materials and Instruments

Chemicals were purchased from Merck and Aldrich chemical companies. All the yields refer to the isolated products. The products were identified by ^{1}H NMR spectroscopy and comparison of their physical constants and spectral data with those reported in literature. The synthesized OIL was characterized by its ^{1}H and ^{13}C NMR (400 MHz) spectra recorded on a Bruker-AVANCE spectrometer. Monitoring of the reaction was performed by TLC on silica gel (polygram SILG/UV 254) plates. Gel-permeation chromatography (GPC) analysis was performed on a Shimadzu LC-20A chromatographer (equipped with Waters Ultrahydrogel Linear column and connected to a RI detector) against polystyrene sulfonate (Na) standards by using 0.1 M solution of $NaNO_3$ as the mobile phase. The TGA (thermogravimetric analysis), DTG (differential thermogravimetry), and DSC (differential scanning calorimetry) studies of the OIL were carried out under He atmosphere on a SETARAM (SETSYS-1760) thermal analyser. The thermal behaviour of the OIL sample (16 mg) was scanned from 40 °C to 600 °C at the rate of 20 °C/min under helium gas flow. Area under each peak in the DSC plot gives an estimate of the enthalpy of the corresponding change which can be calculated by the following equation.

$$\Delta H = \frac{area\ under\ a\ DSC\ peak}{Heating\ rate} \times \frac{1}{16\ mg} = \frac{\mu V.\ ^{\circ}C}{\frac{^{\circ}C}{sec}} = \mu V.sec.mg^{-1}$$

The Fourier transform infrared (FT-IR) spectra were taken by using KBr discs on a Perkin-Elmer Spectrum One apparatus in the range of 400–4000 cm^{-1}. Electrical conductivities were measured on an Orion 101 conductometer using a platinum conductivity cell (cell constant = 1 cm^{-1}).

2.2 Preparation of the OIL; Oligo(imidazolium hydrogensulfate-1,3-diylpropane-2-hydrogensulfate-1,3-diyl)

Imidazole **1** (6 mmol, 0.408 g) and epichlorohydrin **2** (9 mmol, 0.71 mL) were added to absolute ethanol (12 mL) in a round-bottom flask. The resulting solution was stirred for 5-6 h at 60 °C and then was concentrated under reduced pressure to obtain a viscous pale yellow oil. After dilution with dry CH_2Cl_2 (5 mL), sulfuric acid 98% (6 mmol, 0.33 mL) was added in a dropwise fashion over a period of 0.5-1 h at 40-50 °C and under a continuous flow of nitrogen to remove the generated HCl gas. Stirring of the resulting mixture was continued for the next 24 h at room temperature. The supernatant layer (CH_2Cl_2) of the resulting biphasic liquid mixture was decanted and the residual viscous oil was washed with dry CH_2Cl_2 (3 × 5 mL). To this oily residue was added, while stirring, a solution of chlorosulfonic acid (12 mmol, 0.8 mL) in CH_2Cl_2 (5 mL) dropwise over a period of 20 min at 0 °C. Afterward, the resulting mixture was warmed to room temperature and stirring continued for 24 h. The supernatant CH_2Cl_2 layer was decanted and the residue was washed three times with dry CH_2Cl_2 (3 × 5 mL). Evaporation of the volatiles under reduced pressure gave a pale brown oil with lower viscosity than the oil obtained before the sulfonation step (Fig. 1, Scheme 1). GPC analysis of ISA **5** displayed the number averaged molecular weight M_n= 1227 g.mol^{-1}, weight averaged molecular weight M_w= 1328 g.mol^{-1}, and the polydispersity index PDI= 1.08.

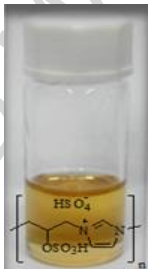


Figure 1. The structure and colour of the synthesized OIL

2.3 General procedure for preparation of pyrano[3,2-*c*]quinolines 10a-h and pyrano[2,3-*d*]pyrimidines 11a-c under catalysis of the OIL

A mixture of an aldehyde **6a-i** (1 mmol), malononitrile **7** (1.1 mmol), 4-hydroxyquinolin-2-one **8**/ 6-hydroxy-tetrahydropyrimidin-4-one **9** (1 mmol), and the above synthesized OIL (0.5 mL) was magnetically stirred under solvent-free condition at 80 °C for an appropriate period of time (according to Table 3). The progress of the reaction was monitored by TLC using n-hexane and EtOAc (in the ratio of 1:1) as eluent. After completion of the reaction, as indicated by TLC, the mixture was cooled at room temperature and distilled water (8 mL) was added while stirring. The solid crude product, which precipitates at this end, was separated from the aqueous layer by decantation and then recrystallized from hot ethanol (95%) to give the pure product. The OIL, remains on evaporation of the aqueous solution

under reduced pressure at 50 °C, was washed with ethyl acetate before use in the next cycle of the same synthesis.

2.4 Selected spectral data for the products

2-Amino-4-phenyl-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile **10a:** IR (KBr): υ_{max} (cm^{-1}) 1381, 1589, 1672, 2206 (C≡N), 3180, 3315, 3462. ^{1}H NMR (400MHz, DMSO-d_6): δ_H 4.49 (1H, s, 4-H), 7.18-7.22 (3H, m, Ar), 7.27-7.32 (5H, m, Ar), 7.34 (1H, d, *J* 8.4Hz, 7-H), 7.58 (1H, dt, *J* 7.6 and 1.4Hz, 8-H), 7.91 (1H, dd, *J* 8.0 and 1.4Hz, 10-H), 11.78 (1H, s, N-H).

2-Amino-4-(4-nitrophenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile **10b:** IR (KBr) υ_{max} (cm^{-1}): 1348 and 1514 (NO_2), 1387, 1632, 1674, 2202 (C≡N), 3335 and 3406 (N-H). ^{1}H NMR (400.13MHz, DMSO-d_6): δ_H 4.69 (1H, s, 4-H), 7.31 (1H, t, *J* 7.6Hz, 9-H), 7.34 (1H, d, *J* 9.2Hz, 7-H), 7.42 (2H, s, NH_2), 7.51 (2H, d, *J* 8.8Hz, 2′- and 6′-H), 7.60 (1H, dt, *J* 7.8 and 1.2Hz, 8-H), 7.93 (1H, d, *J* 8.0Hz, 10-H), 8.17 (1H, d, *J* 8.8Hz, 3′-H and 5′-H), 11.84 (1H, s, N-H).

2-Amino-4-(2-chlorophenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile **10c**: IR (KBr) υ_{max} (cm^{-1}): 1385 (C-O pyran), 1632 (N-H bend), 1674 (C=O), 2195 (C≡N), 3180, 3321, 3365 (N-H). ^{1}H NMR (400.13MHz, DMSO-d_6): δ_H 5.02 (1H, s, 4-H), 7.15 (1H, m, 6′-H), 7.21-7.25 (2H, m, 4′- and 5′-H), 7.27 (2H, s, NH_2), 7.31 (1H, t, *J* 7.6Hz, 9-H), 7.35 (1H, d, *J* 8.4Hz, 7-H), 7.39 (1H, m, 3′-H), 7.59 (1H, t, *J* 7.6Hz, 8-H), 7.92 (1H, d, *J* 8.0Hz, 10-H), 11.74 (1H, s, N-H).

2-Amino-4-(3-bromophenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile **10d**: IR (KBr) υ_{max} (cm^{-1}): 1383 (C-O pyran), 1624 (N-H bend), 1670 (C=O), 2193 (C≡N), 3163, 3360, 3454 (N-H). ^{1}H NMR (400.13 MHz, DMSO-d_6): δ_H 4.54 (1H, s, 4-H), 7.22 (1H, dt, *J* 7.6 and 1.4Hz, 6′-H), 7.27 (1H, t, *J* 7.6HZ, 5′-H), 7.30 (1H, dt, *J* 7.6 and 1.2Hz, 9-H), 7.34 (1H, d, *J* 7.6Hz, 7-H), 7.35 (2H, s, NH_2), 7.39-7.43 (2H, m, 2′- and 4′-H), 7.59 (1H, dt, *J* 7.7 and 1.4Hz, 8-H), 7.91(1H, dd, *J* 8.0 and 0.8Hz, 10-H), 11.81 (1H, s, N-H).

2-Amino-4-(4-chlorophenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile **10e**: IR (KBr) υ_{max} (cm^{-1}): 1383 (C-O pyran), 1674 (C=O), 2187 (C≡N), 3169, 3286, 3379, 3408 (N-H). ^{1}H NMR (400.13MHz, DMSO-d_6): δ_H 4.52 (1H, s, 4-H), 7.24 (2H, d, *J* 8.4Hz

2′- and 6′-H), 7.30 (1H, dt, *J* 8.0 and 1.2Hz, 9-H), 7.32 (2H, s, NH_2), 7.34 (1H, d, *J* 8.4Hz, 7-H), 7.35 (2H, d, *J* 8.4Hz, 3′-H and 5′-H), 7.59 (1H, dt, *J* 7.8 and 1.2Hz, 8-H), 7.91 (1H, dd, *J* 8.0 and 1.2Hz, 10-H), 11.80 (1H, s, N-H).

2-Amino-4-(4-methoxyphenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-*c*]quinoline-3-carbonitrile **10f**: IR (KBr) υ_{max} (cm^{-1}): 1379 (C-O pyran), 1632 (N-H bend), 1676 (C=O), 2183 (C≡N), 3163, 3246, 3283, 3337 (N-H). ^{1}H NMR (400.13MHz, DMSO-d_6): δ_H 3.71 (3H, s, OCH_3), 4.44 (1H, s, 4-H), 6.84 (2H, d, *J* 8.8Hz, 3′-H and 5′-H), 7.12 (2H, d, *J* 8.8Hz, 2′-H and 6′-H), 7.23 (2H, s, NH_2), 7.29 (1H, dt, *J* 7.6 and 1.2Hz, 9-H), 7.33 (1H, d, *J* 8.0Hz, 7-H), 7.57 (1H, dt, *J* 7.8 and 1.6Hz, 8-H), 7.90 (1H, dd, *J* 8.0 and 0.8Hz, 10-H), 11.57 (1H, s, N-H).

2-Amino-4-(4-methylphenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile **10g**: IR (KBr) υ_{max} (cm^{-1}): 1375 (C-O pyran), 1624 (N-H bend), 1691(C=O), 2189 (C≡N), 3223, 3443 (N-H amine). ^{1}H NMR (400.13MHz, DMSO-d_6): δ_H 2.24 (3H, s, CH_3), 4.45 (1H, s, 4-H), 7.08 (4H, s, Ar-H), 7.23 (2H, s, NH_2), 7.29 (1H, dt, *J* 7.6 and 1.2Hz, 9-H), 7.33 (1H, d, *J* 8.0Hz, 7-H), 7.58 (1H, dt, *J* 7.7 and 1.4Hz, 8-H), 7.90 (1H, dd, *J* 8.0 and 1.2Hz, 10-H), 11.76 (1H, s, N-H).

2-Amino-4-(thiophene-2-yl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carbonitrile **10h**: IR (KBr) υ_{max} (cm^{-1}): 1385 (C-O pyran), 1676 (C=O), 2201 (C≡N), 3182, 3319, 3468 (N-H). ^{1}H NMR (400.13MHz, DMSO-d_6): δ_H 4.86 (1H, s, 4-H), 6.93 (1H, dd, *J* 5.2 and 3.4Hz, 4′-H), 6.98 (1H, d, *J* 3.4Hz, 3′-H), 7.29 (1H, dt, *J* 7.6 and 0.8Hz, 9-H), 7.33 (1H, dd, *J* 5.2 and 1.2Hz, 5′-H), 7.35 (1H, d, *J* 8.4Hz, 7-H), 7.40 (2H, s, NH_2), 7.58 (1H, dt, *J* 7.4 and 1.4Hz, 8-H), 7.88 (1H, dd, *J* 8.0 and 1.0Hz, 10-H), 11.88 (1H, s, N-H). ^{13}C NMR (100.61MHz, DMSO-d_6): δ_C 32.1 (C-4), 57.9 (C-3), 110.1 and 112.4 (C-4a and C≡N), 115.9, 120.2, 122.2, 122.6, 124.9, 125.1, 127.4, 131.9, 138.2, 149.1, 151.4; 160.0 and 160.9 (C-2 and C-5).

7-Amino-5-(3-nitrophenyl)-4-oxo-4,5-dihydro-3H-pyrano[2,3-d]pyrimidine-6-carbonitrile **11a**: IR(KBr): υ_{max} (cm^{-1}) 3429, 3326, 3163, 2921, 2185 (C≡N), 1658, 1600, 1396, 1533, 1346 (NO_2). ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 12.80 (1H, s, N-H), 8.18 (1H, s, 2-H), 8.11 (1H, ddd, *J* 8.4, 2.4 and 0.8Hz, 4′-H), 8.05 (1H, t, *J* 2.0Hz, 2′-H), 7.72 (1H, dt, *J* 8.0, 1.4Hz, 6′-H), 7.63 (1H, t, *J* 8.0, 5′-H), 7.33 (2H, s, NH_2), 4.67 (1H, s, 5-H). ^{13}C NMR (100.61MHz,

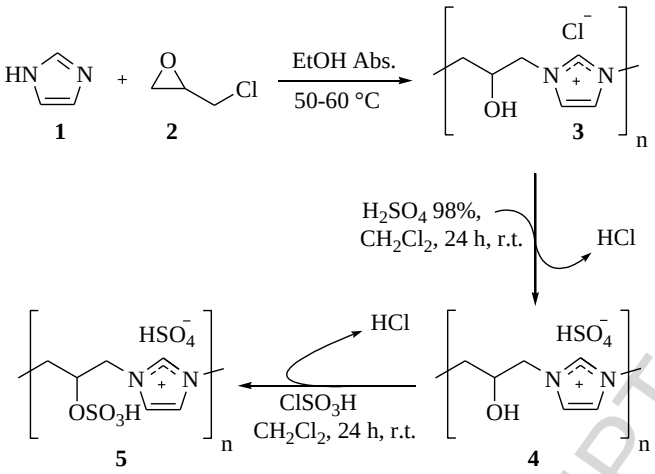
DMSO-d_6) δ_C: 161.1, 160.3, 159.8, 150.5 (C-2), 148.2, 146.5, 134.9, 130.5, 122.5, 119.8 (C≡N), 102.7 (C-4a), 56.6 (C-6), 36.7 (C-5).

7-Amino-5-(2-chlorophenyl)-4-oxo-4,5-dihydro-3H-pyrano[2,3-*d*]pyrimidine-6-carbonitrile **11b**: IR(KBr): υ_{max}(cm^{-1}) 3394, 3326, 2975, 2194 (C≡N), 1658, 1585, 1392. ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 12.72 (1H, s, N-H), 8.16 (1H, s, 2-H), 7.38 (1H, dd, *J* 7.6 and 1.6Hz, 3′-H), 7.28 (1H, dt, *J* 7.6 and 1.6Hz, 5′-H), 7.23 (1H, dt, *J* 7.6 and 2.4Hz, 4′-H), 7.18 (1H, dd, *J* 7.6 and 2.4Hz, 6′-H); 7.16 (2H, s, NH_2); 4.91 (1H, s, 5-H). ^{13}C NMR (100.61MHz, DMSO-d_6) δ_C: 161.0, 160.7, 159.7, 150.2 (C-2); 141.2, 132.7, 130.9, 130, 128.9, 128, 119.7 (C≡N), 102.7 (C-4a), 56.4 (C-6), 34.6 (C-5).

7-Amino-5-(4-chlorophenyl)-4-oxo-4,5-dihydro-3H-pyrano[2,3-*d*]pyrimidine-6-carbonitrile **11c**: IR(KBr): υ_{max}(cm^{-1}) 3417, 3309, 3163, 2920, 2190 (C≡N), 1660, 1587, 1386. ^{1}H NMR (400MHz, DMSO-d_6) δ_H: 12.75 (1H, s, N-H), 8.15 (1H, s, 2-H), 7.36 (2H, d, *J* 8.6Hz, Ar), 7.23 (2H, d, *J* 8.6Hz, Ar), 7.21 (2H, s, NH_2), 4.44 (1H, s, 5-H). ^{13}C NMR (100.61MHz, DMSO-d_6) δ_C: 161.1, 160.1, 159.6, 150.1 (C-2), 143.4, 131.8, 129.8, 128.8, 120 (C≡N), 103.3 (C-4a), 57.2 (C-6), 36.4 (C-5).

3. Results and discussion

As depicted in scheme 1, the reaction of imidazole **1** and epichlorohydrin **2** results in formation of the ionene **3**. Treatment of this ionene with concentrated sulfuric acid in dichloromethane solution resulted in liberation of gaseous HCl and gave the ionene **4** in which the Cl^- counter ions were replaced by HSO_4^- anions. Subsequent addition of ionene **4** to dichloromethane solution of chlorosulfonic acid was also accompanied with liberation of gaseous HCl. This observation was taken as a sign of condensation between these two reacting species, which quantitatively delivered the ionene sulfuric acid (ISA) **5**, i.e. oligo(imidazolium hydrogensulfate-1,3-diylpropane-2-hydrogensulfate-1,3-diyl). The structure assigned to the synthesized ISA **5** is consistent with its FT-IR, ^{1}H- and ^{13}C NMR spectra. A strong sharp band is seen in the FT-IR spectrum of this ISA at 1175 cm^{-1}, corresponding to asymmetric stretching vibration of its SO_4H groups. The strong broad band observed at around 2500–3500 cm^{-1} is relating to O-H stretching vibration of SO_4H group and affirms the presence of this group in the synthesized ISA. Moreover, this spectrum exhibits a band at 1633 cm^{-1} due to C=N stretching vibration of the imidazolium rings.



Scheme 1. An outline of the steps taken for synthesis of the ISA **5**

The ^{1}H NMR spectrum of this ISA in DMSO-d_6 (as solvent) displayed a characteristic peak at 13.95 ppm, which was readily conceived as arising from a portion of the acidic O-SO_3H protons of the OIL. The another part of these protons joined with those of HSO_4^- ions involved in hydrogen bonding with a trace of H_2O impurity of the solvent and appeared at 8.68 ppm. Both of these signals disappeared on exchange of the acidic protons with D_2O and replaced by the signal of HOD at 5.24 ppm. It is noteworthy that the signals of all the C-H protons remarkably shift to upper fields in D_2O (solvent) when are compared with the same signals in DMSO-d_6 (Fig. 2). This shift, which amounts to about 1 ppm, reasonably attests to a conformational change of the oligomeric chain on going from protic to aprotic polar solvent. In D_2O, the HSO_4^- anions are more strongly solvated than in DMSO, largely by hydrogen bonding, hence depart from the oligomeric matrix to gain increased entropy, though, as hydrated anions in solution. As a result, the oligomeric chains are left with several positive point charges positioned along their backbones. Electrostatic repulsions between these charges force the multicationic chain to adopt a rod-like conformation. Upon adopting this spatially extended conformation associated with detachment of the HSO_4^- counter ions, the oligomer is partially relieved from steric constraints and hence it's ^{1}H- and ^{13}C-signals shift to higher fields. On the other hand, due to poor solvation of anions in DMSO-d_6, the oligomeric chain remains entirely screened by HSO_4^- anions and presumably adopts a sterically hindered coil-like conformation in this solvent. For this reason, the ^{1}H and ^{13}C nuclei of the oligomer experience a rather increased steric hindrance in DMSO and their signals shift to lower fields. Like most oligomers, ISA **5** normally consists of chains with different degrees of polymerization. Moreover, even in a single chain, the monomers owing

to their different positions along the molecule may no longer be equivalent, so are expected to display signals at slightly different chemical shifts. In D_2O solution, the 2-H protons (H^f) of the chemically nonequivalent imidazolium units give multiple singlets at δ 7.65-7.92 and the 4,5-H protons of these units along with the geminal proton of the OSO_3H group are seen at 6.45-6.62 ppm. A doublet of AB-quartet (with ^2J = 12 Hz and ^3J = 4.6 Hz) which appears at up-field (δ_H 2.71 and 2.67) of this spectrum (in D_2O) is assigned to the diastereotopic protons of the terminal methylene (CH_2-Cl) groups (Fig. 2). These signals are interesting in that significantly shift to lower fields (δ_H 3.52 and 3.47) in DMSO-d_6 and their integrated intensity, with respect to that of the remaining aliphatic protons, gives an estimate of the degree of polymerization (dp) for ISA **5**. Considering that application of excess epichlorohydrin gives the linear ISA **5** symmetrically capped with CH_2-Cl groups, the dp of this polymer can be calculated by the following equation:

$$\frac{\boldsymbol{m(\bar{P}_n+1)-n}}{\boldsymbol{n}} = \frac{\boldsymbol{I_i}}{\boldsymbol{I_j}}$$

where $\bar{P}_n$ denotes the number-averaged dp for ISA **5**, *m* refers to the number of aliphatic protons present in each repeating unit, and *n* is the total number of the terminal CH_2-Cl protons in each polymeric chain. The two symbols I_i and I_j stand for the integral intensity of the signals arising from the internal aliphatic protons ($^+$N-CH_2 and O-CH appearing at δ_H 3.24-3.57) and the terminal methylene protons n, respectively. Upon determining the value of I_i/I_j = 4.8 from ^{1}H NMR spectrum of ISA **5** and substituting it into above equation and given that for most ISA **5** chains *m* = 5 and *n* = 4, we obtain $\bar{P}_n = 3.64$ for this OIL. The oligomeric structure of ISA **5** is also supported by its GPC (gel permeation chromatography) analysis which displays a unimodal size-distribution with number averaged molecular weight of M_n= 1227 g.mol^{-1} and polydispersity index of PDI= 1.08. These values correspond to a narrow size-distribution of the oligomeric molecules with $\bar{P}_n$= 3.37 and are in good agreement with the result obtained from the ^{1}H NMR study of the OIL. The slight difference between the $\bar{P}_n$ deduced from the ^{1}H NMR measurement and that from the GPC analysis ($\Delta\bar{P}_n$= 0.27) is due to a minute non-oligomeric condensation products, which are eluted within a longer time as a unimodal weak peak separate from the main GPC curve.

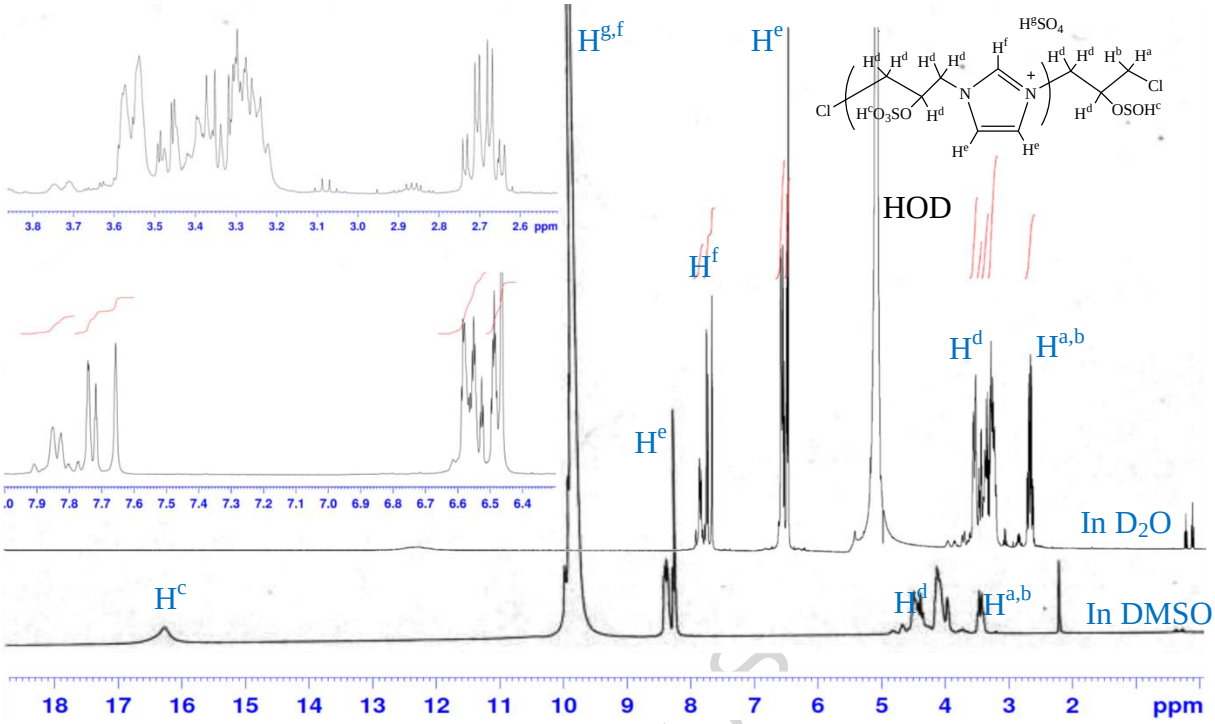


Figure 2. ^{1}H NMR spectra of the ISA **5** in D_2O and DMSO

Similar shifts to lower fields were observed for the ^{13}C NMR signals of this OIL on transferring from D_2O to DMSO-d_6. The magnitude of this shift is somewhat greater for the carbon nuclei of the imidazolium rings than that of the aliphatic carbons. Probably, the large deshields of the imidazolium carbons is somehow attributed to the steric requirements of their proximate HSO_4^- anions. Moreover, the NMR spectra of the ionenes **3** and **4** show that the chemical shifts of ^{1}H and ^{13}C nuclei in these oligomers considerably vary by exchanging the counter anion Cl^- with HSO_4^- and sulfonation of the OH groups. Other details regarding the ^{1}H NMR and ^{13}C NMR signals are provided in the supporting information of this article.

Thermal behaviour of the synthesized ISA **5** was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the temperatures between 25 to 600 °C (Fig. 3). Three weight loss stages are observed in the TGA of the sample. The first step in the TG curve, which starts at the onset point of 125 °C corresponds to an endothermic trace, centring at 155 °C, in the DSC thermograph of the polymer and is followed by two additional mass loss steps occurring at the ranges (220−280 °C) and (320-365 °C) of the TG analysis. These two latter steps, where appearing in the DSC curve of ISA **5** at 250 °C and 345 °C, are likewise endothermic in nature but have the enthalpies much lower than that of the first step. After these three steps, which are explicitly recognizable from the differential thermogravimetric (DTG) analysis, the oligomer undergoes a smooth decomposition at temperatures greater than 365 °C to complete

weight loss. The DSC trace of the oligomer in the temperature interval of this late decomposition stage shows an exothermic peak occurring at 514.9 °C (Fig.3).

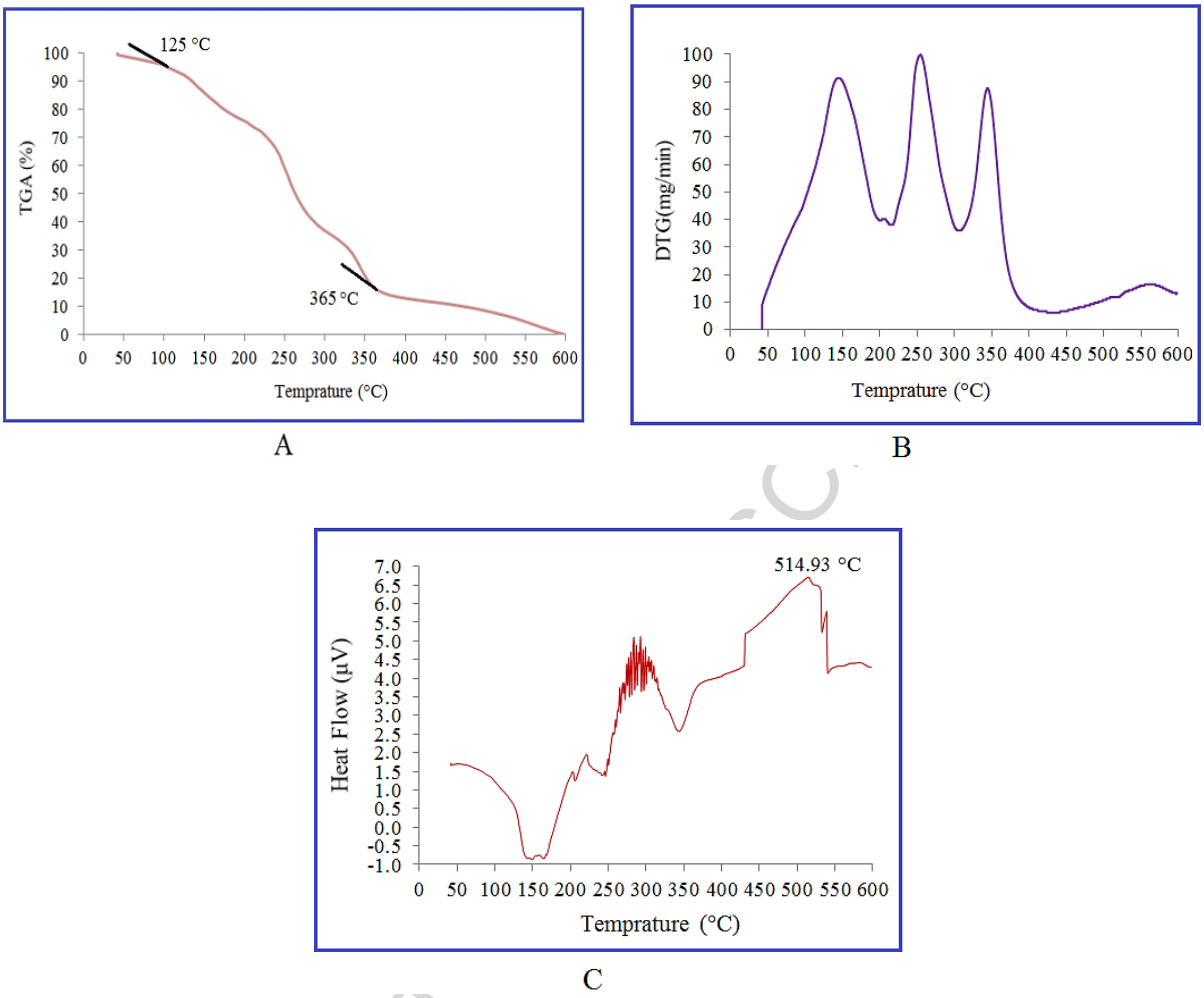
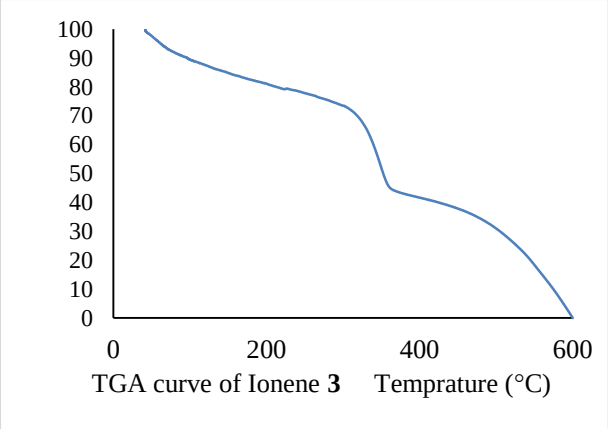


Figure 3. The thermograms TGA (A), DTG (B), and DSC (C) of the ISA **5**

In sharp difference to ISA **5**, the ionenes **3** and **4** have shown greater thermal stabilities (Fig. 4). The TGA curve of **3** exhibits only one main decomposition step, starting at the onset point of 315 °C, whilst those of ionene **4** and ISA **5** consist of two and three main decomposition steps and the onset points of their early steps occur at 230 °C and 125 °C, respectively. Noticeably, all of these ionenes (**3**, **4**, and **5**) have a common endothermic decomposition trace in their TGA curves, which gives a peak at around 348 °C. Based on these thermograms one may suggest that the two early decomposition steps of ISA **5** stem from its HSO_4 substituents and HSO_4^- anions.

(%) (%)



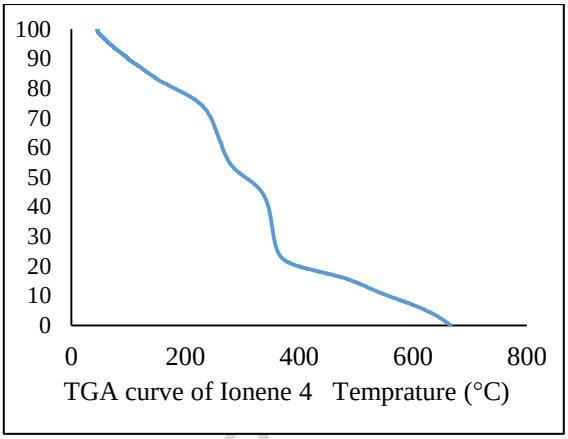


Figure 4. The TGA curves of the ionenes **3** and **4**

Owing to possessing HSO_4 groups as both counter anion and substituent, ISA **5** is a Brønsted acidic OIL. An estimate of the acidic strength that is produced by this liquid oligomer in non-aqueous media can be calculated by Hammett's acidity function [18]. This function is expressed by the following equation:

$$H_o = pK_a(BH^+)_{aq} + \log ([B] / [BH^+])$$

where $pK_a(BH^+)_{aq}$ denotes the pK_a of an indicator base in aqueous solution and $[B]/[BH^+]$ stands for the molar concentration ratio of the indicator to its conjugate acid in non-aqueous media. Here, 4-nitroaniline (with pK_a = 0.99) was chosen as the indicator base and the value of $[B]/[BH^+]$ was determined by measuring the UV-visible absorbances of 4-nitroaniline at the maximal absorption wave length (λ_{max}) of 335 nm before and after adding ISA **5** to its solution in CCl_4 (Fig. 5). As Table 1 shows, the data obtained from these evaluations afford the value of H_o = 0.59 for ~2 $g.L^{-1}$ of the ISA **5** in CCl_4.

Table 1. The absorbances measured at λ_{max}= 335 nm for determining the Hammett's acidity value (H_0) of the synthesized ISA **5** in CCl_4 [a]

Entry	Acid	A_{max}	[B] (%)	$[BH^+]$ (%)	H_o
1	-	1.139	100	0	-
2	ISA **5**	0.324	28.44	71.55	0.59

[a] The conditions adopted for UV–visible measurements in CCl_4: 1.44×10^{-4} mol/L solution (10 mL) of 4-nitroaniline ($pK_a(BH^+)_{aq}$= 0.99) as the base indicator; ISA **5** (the OIL, 20 mg); 25 °C.

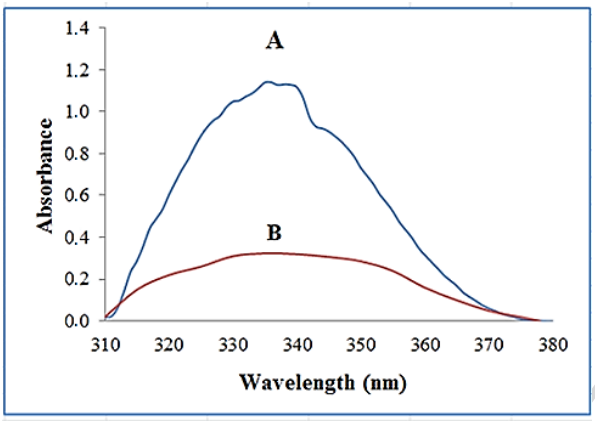


Figure 5. The UV-visible absorption spectra of 4-nitroaniline in CCl_4 (A), and after addition of the ISA **5** (B)

In Table 2 the acidic strength of ISA **5** was compared with those of some mineral and organic acids in the Hammett's scale. As can be seen, the acidic strength of ISA **5** is comparable to that of 0.25 M H_2SO_4 (aq) and is far greater than most reported acidic ionic liquids.

Table 2. The Hammett's acidity values for ISA **5** and some selected acids

Acid	H_2SO_4[a]	CF_3SO_3H	$[Gly]NO_3$	$[BMIm]HSO_4$	$[HMIm]BF_4$
H_o	0.45 [19]	-13.7 [20]	2.44 [21]	0.8 [22]	1.28 [22]

[a] 0.25 M aqueous solution.

ISA **5** exhibits significant electric conductivity (EC) in both DMSO and water as a signature of its ionic character. Figure 6 displays the temperature-dependent plots of the electrical conductivity owned by ISA **5** in DMSO and water. To assess the conductivity owned by ISA **5** in each of the solutions, we made the following calculation:

$$\Lambda_{(t,ISA)} = \Lambda_{(t,solu.)} - \Lambda_{(t,solv.)}$$

where $\Lambda_{(t,ISA)}$ stands for the contribution of ISA **5** to EC of its solution at a given temperature and the symbols $\Lambda_{(t,solu.)}$ and $\Lambda_{(t,solv.)}$ refer to conductivities of the solution and the blank solvent at the same temperature, respectively. It is evident that ISA **5** makes a larger contribution to EC of its solution in DMSO than in water. This difference shows that the oligomeric chains have a restricted mobility in water arising from their extensive hydrogen bonding with solvent and so greater Stokes radii in water than in DMSO. The greater Stokes radii of ISA **5** chains in water may also be due to the rod-like shape that they adopt in this solvent. Upon rising the temperature, the EC of ISA **5** in water increases, however, with a far lower slope than in DMSO. The sharp effect of temperature on the EC of ISA **5** in DMSO is

related, inter alia, to removal of less-bound solvent molecules from its chain at higher temperatures and to remarkable conformational folding of the multicationic chains in this solvent, making the multicationic ISA more mobile. The increasing mobility of the conjugated anions at elevated temperatures also heightens the EC of the DMSO solution whereby it reaches to a maximum at 67 °C. Above this temperature, the conductance curve follows a fairly constant decreasing trend, presumably, due to aggregation of the polymeric chains and consequently a decrease in the number of ions per volume of solution.

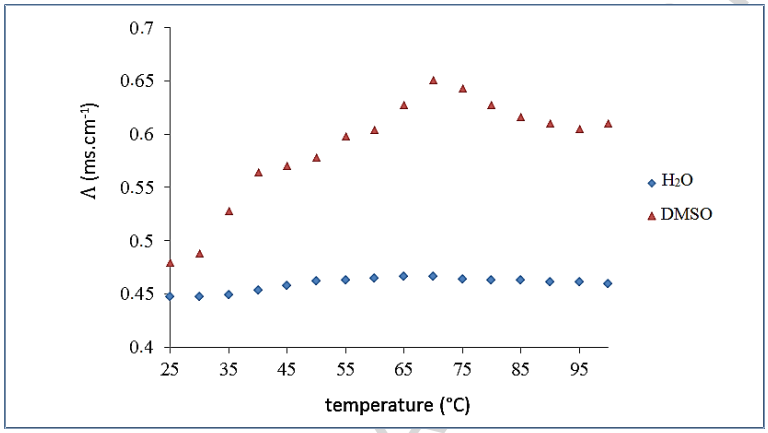
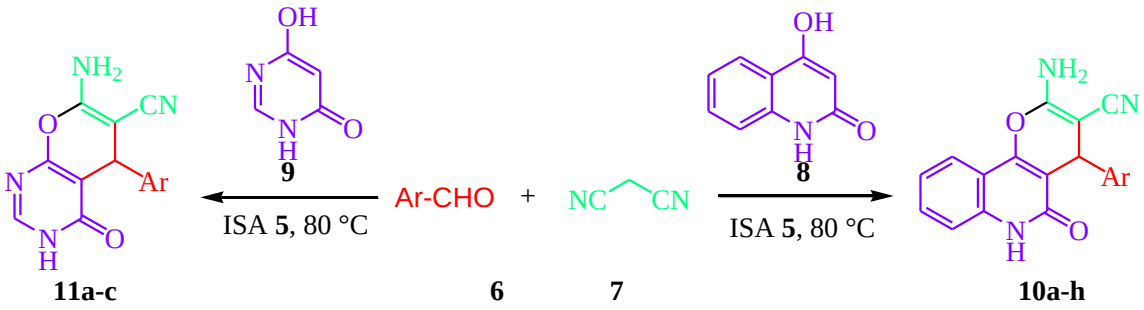


Figure 6. Plots of conductivity (Λ) against temperature for ISA **5** in H_2O and DMSO

Based on its acidic and ionic-liquid nature, the ISA **5** is expected to play as an effective medium especially for the acid demanding reactions. In this view, we planned to examine the utility of ISA **5** in the synthesis of pyrano[3,2-*c*]quinolines and pyrano[2,3-*d*]pyrimidines *via* the three-component reaction of 4-hydroxyquinolin-2-one **8**/6-hydroxy-tetrahydropyrimidin-4-one **9** with malononitrile **7** and arylaldehydes. For this purpose, the reaction between 4-hydroxyquinolin-2-one **8**, malononitrile **7**, and benzaldehyde **6a** in the presence of ISA **5** was chosen as the model reaction. Initial results of our attempts to find out the optimum conditions for the trial synthesis of **10a** were encouraging in terms of yields and reaction times. The best results for the model reaction were obtained at 80 °C using 0.5 mL of ISA **5** per 1.1 mmol of malononitrile **7** and 1 mmol of each of the other reactants.

In next phase of this investigation we set out to examining the substrate scope of the method by employing different substituted aromatic aldehydes (Table 3, Scheme 2). As Table 3 shows, this synthetic method has no appreciable sensitivity to presence of various substituents and goes almost equally well with electron-rich and electron-deficient as well as sterically hindered aromatic aldehydes to give the desired products. Beside its role as an acidic catalyst, ISA **5** also plays as solvent. Hence, all the syntheses underwent smoothly in homogeneous phase.



Scheme 2. Three-component one-pot synthesis of pyrano[3,2-*c*]quinolines **10a-h** and pyrano[2,3-*d*]pyrimidines **11a-c** under catalysis of ISA **5**

Table 3. The representative syntheses of pyrano[3,2-*c*]quinolones **10a-h** and pyrano[2,3-*d*]pyrimidines **11a-c** under catalysis of ISA **5** at 80 °C

Product	Ar	Time (min)	Yield (%)[a]	Mp ^{Found} (°C)	Mp $^{Lit.}$ (°C)
10a	Phenyl	10	90	297-299	>300[14]
10b	4-Nitrophenyl	5	92	>300	>300[14]
10c	2-Chlorophenyl	15	84	294-296	>300[14]
10d	3-Bromophenyl	10	89	>300	>300[13a]
10e	4-Chlorophenyl	10	88	297-299	>300[14]
10f	4-Methoxyphenyl	15	83	297-300	>300[14]
10g	4-Methylphenyl	10	90	>300	>300[14]
10h	Thiophen-2-yl	10	83	>300	>300[13a]
11a	3-Nitrophenyl	10	92	291-293	273-275[13b]
11b	2-Chlorophenyl	20	80	276-278	263-265[13b]
11c	4-Chlorophenyl	15	85	273-275	254-256[13b]

[a]Isolated yields

A comparison of ISA **5** and some previously reported catalysts for synthesis of the model product **10a** was presented in Table 4. It is evident from this table that ISA **5** can be represented as an efficient catalyst for the synthesis of pyrano[3,2-*c*]quinolin-4-ones. Although ammonium acetate is a cheap and efficient catalyst for the synthesis of the model product (entry 4), it cannot be recovered completely from the reaction mixture, due to decomposition in hot solutions *via* the loss of ammonia. The other catalysts either result in lower reaction rate (entry 2) or need a complicated procedure, including fine filtration, for separation from the products (entry 1).

Table 4. A comparative catalytic efficacy of ISA **5** for synthesis of the model product **10a**

Entry	Catalyst	Time	Yield (%)[a]	Conditions	Ref.

1	$(CTA)_3[SiW_{14}]$-Li^+-MMT	10 min	93	Reflux/ H_2O	[23]
2	KF-Alumina	5 h	78	Reflux/ EtOH	[24]
3	DABCO	20 min	87	Reflux/ H_2O:EtOH (1:1)	[25]
4	Ammonium acetate	3 min	94	Reflux/ EtOH	[14]
5	The ISA **5**	10 min	90	80 °C, Solvent-free	This work

[a]Isolated yields

Solubility of ISA **5** in common solvents would be a matter of interest as it throws light on choice of a suitable procedure for separation of this OIL from the reaction mixtures. Table 5 exhibits that ISA **5** is insoluble in common nonpolar solvents, as a consequence of its ionic and polar groups.

Table 5. Solubility of ISA **5** in common selected solvents

Solvent	At 25 °C	Hot [a]
CH_2Cl_2	Insoluble	Insoluble
$CHCl_3$	Insoluble	Insoluble
EtOH	Less soluble	Soluble
H_2O	Soluble	Soluble
AcOEt	Insoluble	Insoluble
Acetone	Insoluble	Insoluble
DMSO	Soluble	Soluble

[a]At 60 °C except for CH_2Cl_2 (35 °C) and acetone (55 °C).

Reusability and recycling performance of ISA **5** was examined for production of compound **10a** at 80 °C. It was found that the recovered oligo(ionic liquid) could be reused directly in the next run without appreciable loss of activity even after four times recycling (Fig. 7).

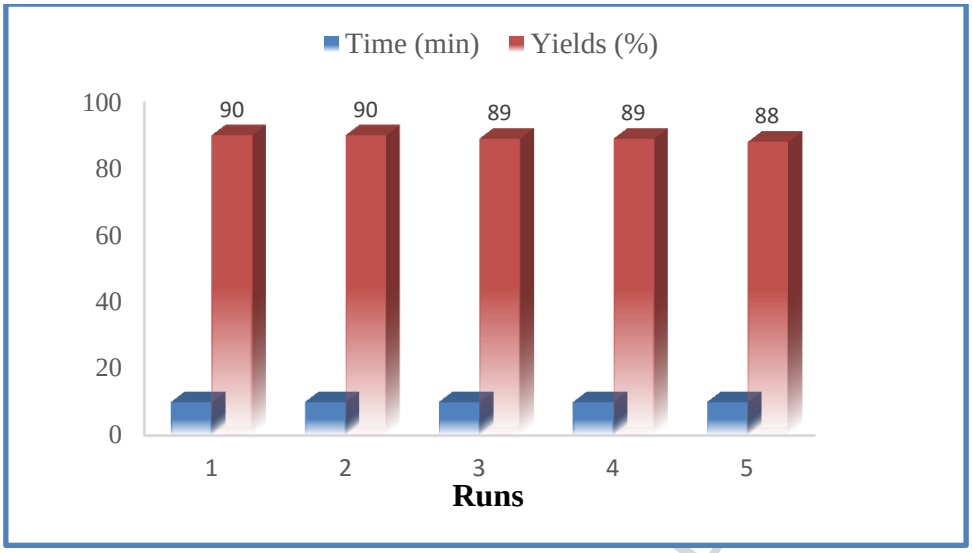


Figure 7. The reusability of ISA **5** in synthesis of (**10a**) at 80 °C

Conclusion

Co-oligomerization of imidazole with epichlorohydrin led to formation of a light 1,3-ionene, which on sulfonylation with chlorosulfonic acid and subsequent anion exchange with sulfuric acid gave the ionenesulfuric acid ISA **5**. The ^{1}H and ^{13}C NMR spectra of this ionene are consistent with its oligo(ionic liquid) structure and displayed a conformational change when ISA **5** was transferred from D_2O to DMSO, as a sign of its multicationic nature. The liquid ISA was proved to be a highly efficient Brønsted acidic promoter for synthesis of pyrano[3,2-*c*]quinolines and pyrano[2,3-*d*]pyrimidines *via* a simple one-pot protocol under solvent-free conditions to give fairly high yields in short reaction times. The oligo(ionic liquid) can be reused several times without sensible loss of activity.

Acknowledgements

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Highlights

A liquid ionene, bearing HSO_4 counter anion and substituent, was synthesized► The ionene has a flexible conformation responding to solvent changes► It seems to take a rod-like conformation and resists to folding by heating in water► The ionene was applied as a catalyst for synthesis of some pyran-annulated quinolines and pyrimidines► The ionene has a long-term stability and can be recycled several times.