Comparison between polymerized ionic liquids synthesized using chain-growth and step-growth mechanisms used as stationary phase in gas chromatography

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Abstract

In this study the merits of polymerized imidazolium based ionic liquid (PIL) stationary phases obtained via condensation and free radical polymerizations are compared as stationary phases in gas chromatography (GC). Poly(1-vinyl-3-butyl-imidazolium – bis(trifluoromethane)sulfonamide) (poly(ViC$_4$Im$^+$ NTf$_2^-$)) was obtained via a chain-growth mechanism while poly(propylimidazolium-NTf$_2$) (poly(C$_3$Im$^+$ NTf$_2^-$)) was synthesized via a step-growth polymerization. The thermal stability of both polymers was assessed using thermal gravimetric analysis and compared with bleeding profiles obtained from the statically coated GC columns (30 m x 0.25 mm x 0.25 μm). The performance was compared to what could be obtained on commercially available 1,5-di(2,3-dimethylimidazolium)pentane^{2+} 2NTf$_2^-$ (SLB-IL111) ionic liquid based columns. It was observed that the step-growth polymer was more thermally stable, up to 325°C, while the chain-growth polymer showed initial degradation at 250°C. Both polymers allowed reaching minimal plate heights of 0.400 to 0.500 mm for retained solutes such as benzaldehyde, acetophenone, 1-methylnaphthalene and aniline. Assessment of the McReynolds constants illustrated that the polarity of the step-growth polymer was similar to the SLB-IL111 column, while displaying improved column stability. The PIL phases and particularly the so far little studied condensation based polymer shows particular retention and satisfactory column performance for polar moieties such as esters, amine and carbonyl functionalities.

Keywords

Highlights

- Imidazolium based polymeric ionic liquid phases were manufactured.
- Polymers obtained via chain- and step-growth mechanisms were prepared.
- Step-growth polymer showed excellent thermal stability as stationary phase.
- Optimal plate heights down to 0.4 mm were obtained on 0.25 mm columns.
- The high polarity and broad applicability of the phases was demonstrated.

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1.   Introduction

Since the notion of capillary columns was introduced by Golay in 1957, allowing for vastly improved efficiencies compared to what is achievable with packed columns, wall coated open tubular columns (WCOT) have become the predominant column choice in gas chromatography. This approach was aided by the introduction of efficient coating processes [1], deactivating wall treatments procedures and stationary phases depicting increasing temperature stability. Most of the purchased columns today possess a thin layer of temperature stable polymer, which can be used for a wide variety of applications and which, in the case of polydimethylsiloxane (PDMS), allows for operation temperatures of up to 430°C to be reached [2]. However, when alternative separation selectivity is required, for example, towards the separation of polar or isomeric molecules, these phases often don't offer satisfactory solutions [3,4]. The main disadvantage of the traditional polar phases, which have been developed for those purposes such as phenyl, cyanopropyl modified PDMS and polyethyleneglycol (WAX), is their decreasing maximum operating temperature, down to 250°C for cyanopropyl (HP-88) based columns and 280°C for most polar WAX phases. Therefore the introduction of ionic liquids (IL) as more stable alternatives has been promising as especially the latter substantially addresses the temperature stability issues of the most polar phases [5]. In this way highly polar commercial ionic liquid based phases can now be used up to 300°C.

The ionic liquids (ILs) considered interesting for chromatographic purposes are typically a class of organic molecules consisting of an organic cation combined with a negatively charged organic or inorganic counterion. Ionic liquids possess no notable vapour pressure and can in some cases be thermally stable up to 350-380°C [5], while being chemically and electrochemically stable, even towards harsh acids and bases. Moreover, ionic liquids are non-flammable, have a high heat capacity and most of them are considered liquid at room temperature. This low melting point is due to the larger size of the cation compared to the anion inhibiting the possibility to fit into a crystalline structure. These liquid salts are able to dissolve a wide range of organic and inorganic salts, while being miscible with water and most organic solvents. Typical cations include imidazolium, pyridinium, alkylammonium and pyrrolidinium groups, while the most common anions are halides, hexafluorophosphate (PF_6^-) or organic anions such as bis(trifluoromethane)sulfonimide (NTf_2^-). The properties of the ionic liquid can be easily tuned by varying the cation and anion. One of the most interesting cations concerning its thermal stability is the imidazolium group, since the ring structure can divide the extra energy coming from the increasing temperature. Variations in anion type influence the hydrophobicity and thus its solubility as well as the thermal stability. Halide containing ILs are soluble in water, while NTf_2^- and PF_6^- anions make the structure insoluble in water. A similar trend is observed considering the thermal stability, where it increases using NTf_2^- and PF_6^- as counterion, compared to halide anions [6]. All the above mentioned characteristics have made the applications of IL numerous, especially in chemical analysis [7,8] whereby research has been conducted on the use of ionic liquids as extractive phase for SPME [9–13], as stationary phase in GC [14–17], LC [18–20] and as wall coating material in capillary electrophoresis [21–23].

Ionic liquid GC columns have been commercialized and are increasingly implemented [24,25]. A limited number of ionic stationary phases are available, all possessing the same NTf_2^- counterion, or mixtures of NTf_2^- and trifluoromethylsulfonate (Tf^-) anions. The commercialized IL phases typically contain cationic di- or trimer moieties linked by lengthy spacer segments. The more polar stationary phases possess an imidazolium cation (SLB-IL82,100,111) while the intermediate polarity columns depict phosphonium groups (SLB-IL59,60,61,76). As expected, the shorter the linker, the higher the polarity of the column, as can be seen when comparing SLB-IL111 with SLB-IL82, both depicted in Figure 1A. The thermal stability of these very polar stationary phases ranges from 230°C to 300°C. Some PEG linked imidazolium phases have been reported that allow operating ranges up to 350°C

113 [16]. The non-polymerized phases appear to some extend somewhat limited in terms of low viscosity
114 at high temperatures and regarding thermal stability. Through the addition of a polymerizable unit to
115 the cation and/or anion structure, polymeric ionic liquids (PILs) were introduced. Atop the enhanced
116 viscosity, these polymers possess excellent thermal stability, combined with the characteristics of an
117 ionic liquid and typical polymer properties such as improved mechanical stability and processability
118 [26,27]. Poly(ionic liquid)s can be divided into two categories based on the way the polymerization is
119 achieved: chain-growth PILs (Figure 1B) and step-growth PILs (Figure 1C) [27,28]. In the former case,
120 the cationic moiety is present in the side-chain of the polymer structure. Since the monomer
121 structure resulting in these polymers can be altered in many ways, this is by far the largest group.
122 First of all, the polymerizable unit can either be vinyl, (meth)acryloyl or a styrene based structure
123 [29–31]. All these monomers result in polymers with similar thermal stability ranging between 300°C
124 and 340°C. The polymerization is started by adding a suitable radical initiator like AIBN and heating
125 upon dissociation hereof. Secondly, there is a wide variety in cationic moieties. Phosphonium and
126 imidazolium cations are used in most cases, as these possess the highest polarity, combined with
127 excellent thermal properties. Thirdly, in order to effectively obtain a cationic function on phosphor or
128 imidazole, an additional alkyl or similar substituent is needed, which as mentioned, affects the
129 intrinsic polarity. The choice of the counterion is also critical as this has strong influence on the
130 thermal stability. During the synthesis of the monomer, a halide anion is typically present. As was
131 described by Kroon et al. this ion induces undesired reactions at elevated temperatures [32]. It could
132 thereby be shown that ionic liquids such as butylmethylimidazolium chloride ($BMIM^+$ Cl^-) can
133 thermally decompose due to an S_N2 reaction of the nucleophilic chloride anion on the methyl-group,
134 resulting in dealkylation of the cation and the formation of chloromethane and butylimidazole.
135 Similar reactions can be expected in polymers where either removal of alkyl substituent or a rupture
136 of the polymer backbone, result in the loss of a cation in the polymeric structure. Even though these
137 halide counterions introduce the highest polarity, the mentioned reactions make them less desirable
138 for high temperature applications. Therefore the ion is typically exchanged for an NTf_2^- or a similar
139 counterion. These counterions don't induce dealkylation reactions, but at higher temperatures
140 thermal decomposition of NTf_2^- with the formation of sulphur dioxide still occurs [6,32]. Polymerized
141 ionic liquids based on this structural pattern have been applied in sample preparation techniques
142 [33–35] as well as for stationary phase in gas chromatography [36,37].

Figure 1

144 The second group of polymeric ionic liquids is formed via a step-growth polymerization. Here the
145 cationic moiety is present in the polymeric chain itself. No catalyst is needed as the polymerization
146 takes places by increasing the temperature. The typical polymer structure is shown in Figure 1C. In
147 order to increase the thermal stability, the halide counterion is thereby also exchanged for an NTf_2^-
148 or similar anion. This polymer can reach higher thermal stabilities up to 400°C and has been tested as
149 stationary phase in GC as well by Ho et al. [38,39] on somewhat shorter columns coated with thin
150 polymer films (10 m x 0.25 mm x 0.20 μm).

151 To allow for a one on one comparison of the condensation type polymer with the one obtained via
152 free radical polymerisation in this work both types are synthesized and characterized using thermal
153 gravimetric analysis (TGA) and NMR. Subsequently these polymers are coated in a similar way using
154 the static coating method to obtain stationary phases in 30 m long capillary columns of 0.25 mm
155 internal diameter for fundamental and practical evaluation of the respective gas chromatographic
156 performance, whereby comparison is made with the performance of a commercial IL column. In
157 order to do so, thermal stability is studied by recording bleeding profiles and the van Deemter curves
158 for representative retained compounds are constructed (benzaldehyde, acetophenone, 1-

159 methylnaphthalene and aniline). Additionally, the selectivity is studied by analysing a number of test
160 mixtures containing molecules with different functionalities and polarity. In this way, the polarity by
161 means of McReynolds constants is determined. As a case study, a mixture containing 37 fatty acid
162 methyl esters (FAMEs) was analysed on the condensation type polymeric stationary phase.

163

2.   Experimental procedure

2.1.   Reagents and materials

166 Imidazole, 1-bromo-3-chloropropane, lithium hydride, bis(trifluoromethane)sulfonimide lithium salt,
167 1-vinylimidazole, 1-bromobutane, 2,2'-azo-bis(isobutyronitrile) (AIBN), nonane, decane, undecane,
168 dodecane, tridecane, pentadecane, hexadecane, docosane, decalin, mesitylene, 1,3,5-tri(t-
169 butyl)benzene, 1-methylnaphthalene, 1-butanol, 2-pentanone, benzene, pyridine, 1-nitropropane,
170 aniline, benzaldehyde, acetophenone, THF (distilled in-house over sodium), methylenechloride,
171 acetone, methanol, 2-propanol, ethylacetate, DMF (dried in-house over molecular sieves), 37
172 component FAME mix (10 mg/ml in methylene chloride), linoleic acid methyl ester isomer mix (10
173 mg/ml in methylene chloride), the SLB-IL111 column (30 m x 0.25 mm x 0.2 μm d_f) and bare non-
174 deactivated fused silica with an internal diameter of 0.250 mm were obtained from Sigma-Aldrich
175 (Bornem, Belgium). Tetradecane, heptadecane, bicyclohexyl and butylcyclohexane were purchased
176 from TCI Europe (Zwijndrecht, Belgium). Water (18.2 MΩ/cm) was purified and deionized in house
177 via a Milli-Q plus instrument from Millipore (Bedford, New Hampshire, USA). DB-WAX (30 m x 0.25
178 mm x 0.25 μm d_f) was obtained from Agilent Technologies (Diegem, Belgium). Stock solutions of all
179 compounds were prepared at 10 mg/ml in dichloromethane and diluted herein to 1000 and 100
180 μg/ml for the Van Deemter and selectivity studies, respectively.

2.2.   Synthesis of PIL obtained using a step-growth mechanism: Poly(propylimidazolium - bis(trifluoromethane)sulfonimide) (poly($C_3Im^+ NTf_2^-$))

183 The polymeric ionic liquid formed via a step-growth mechanism was synthesized using the reaction
184 scheme shown in Figure 2, adapted from Amarasekara et al. [40]. The monomer was produced as
185 followed: 0.046 mol imidazole, dissolved in 25 ml dry THF, was added slowly to a suspension of
186 lithiumhydride (0.046 mol) in 25 ml dry THF and stirred for 90 minutes at 0°C, under nitrogen
187 atmosphere in a 250 ml round bottom two-neck flask. Next 1-bromo-3-chloropropane (0.046 mol)
188 was added dropwise at 0°C and the resulting mixture was stirred at room temperature for 24 hours.
189 In order to terminate the reaction, 100 ml of water was slowly added, as hydrogen gas was formed
190 during this process. The monomer was extracted with 3 times 75 ml dichloromethane, which was
191 dried over Na_2SO_4. After filtration, the solution was concentrated with a rotary evaporator using a
192 water bath at room temperature. The resulting oil was stored in the freezer to prevent self-
193 polymerization.

194 The subsequent polymerization was done in a straightforward way as no initiator was thereby
195 needed. The monomer only required heating to 110°C, under inert atmosphere in a pressure vial, in
196 order to perform a step-growth polymerization. As no side product is formed during an addition
197 polymerization, no extensive clean-up was required. The resulting white solid was dissolved in little
198 methanol. This solution was then poured into an excess of acetone, resulting in a white precipitate
199 that was filtered on a por. 5 glass filter obtained from Robu® Glasfilter-Geräte GmbH (Hattert,
200 Germany). The resulting powder was dried for 1 day in an oven at 60°C. The polymer was stored in a
201 desiccator under vacuum, as poly($C_3Im^+ Cl^-$) is hygroscopic by nature.

202 In order to significantly improve the thermal stability of the polymer, the chloride counterion was
203 exchanged for a bis(trifluoromethane)sulfonimide (NTf_2^-) ion. Therefore, 3 gram of polymer (0.021
204 mol) was dissolved in 10 ml water, to which a 3 equivalent excess of $LiNTf_2$ (0.063 mol) dissolved in
205 10 ml water was added and stirred for 24 hours. The resulting precipitation was filtered and rinsed
206 with water, until no more chloride was detected in the rinsing water using $AgNO_3$.

207 **Figure 2**

208 ## 2.3. Synthesis of PIL obtained using a chain-growth mechanism: Poly(1-vinyl-3-
209 butylimidazolium - bis(trifluoromethane)sulfonimide)(poly($ViC_4Im^+ NTf_2^-$))

210 The other PIL was synthesized via a chain-growth mechanism, as shown in Figure 3, based on work
211 from Marcilla et al [41] and Green et al [29]. The ionic liquid monomer is formed in a reaction
212 between 1-vinylimidazole (0.05 mol) and 1-bromobutane (0.06 mol) in ethyl acetate, stirred and
213 refluxed for 16 hours in a 250 ml round-bottom flask, resulting in a separate viscous layer. After
214 decanting and rinsing with 3 times 50 ml ethyl acetate, the product was dried using a rotary
215 evaporator with the water bath at 45°C to remove residual 1-bromobutane and ethyl acetate.

216 Next, 5 gram of monomer (0.022 mol) was dissolved in 20 ml dry DMF and 0.00044 mol of the
217 initiator AIBN was added in a 50 ml round-bottom flask. The solution was purged with nitrogen and
218 subsequently heated to 90°C for 12 hours under nitrogen atmosphere. After completion, the reaction
219 mixture was cooled down to room temperature with the formation of a white precipitate.
220 Additionally, acetone was added to ensure complete precipitation. After filtration, the polymer
221 (poly($ViC_4Im^+ Br^-$)) containing bromide as counterion was obtained.

222 Finally, this bromide ion was exchanged for an NTf_2-ion, in a similar way as described for the
223 condensation polymer in 2.2, resulting in the final poly($ViC_4Im^+ NTf_2^-$).

224 **Figure 3**

225 ## 2.4. Characterization of monomers and polymers
226 NMR data of monomers and polymers were obtained on a Bruker 400 MHz Ultrashield™ and are
227 provided in supplementary information. Thermal gravimetric analyses were performed on a
228 TGA/SDTA851e system (Mettler-Toledo, Zaventem, Belgium) in a temperature range from 25°C to
229 800°C at 10°C/min under N_2-atmosphere (200 ml/min).

230 ## 2.5. GC capillary column coating
231 Both polymers were coated in a capillary column using the static coating method [1]. Therefore the
232 condensation polymer (poly($C_3Im^+ NTf_2^-$)) was dissolved in acetone, while the addition polymer
233 (poly($ViC_4Im^+ NTf_2^-$)) was dissolved in dichloromethane. The applied concentration is depending on
234 the desired film thickness (d_f), which can be calculated using (1) with c = concentration of the
235 polymer solution, d_f = desired film thickness, ρ = density of the polymer and d_c = internal diameter of
236 the column. Here, a film thickness of 0.25 μm was intended in the 0.25 mm capillary column, as
237 solutions had a concentration of 4 mg/g.

$$c = \frac{4 \, d_f \, \rho}{d_c} \qquad (1)$$

238 The 30 m long column was pretreated as followed: first 1M NaOH solution was flushed through using
239 a nitrogen-pressurized glass container, followed by milli-Q water. Next 1M HCl was pumped through
240 the column and rinsed with water, after which methanol was used to remove any water residue
241 present in the column. Finally, the column was rinsed with the solvent used for dissolving the

subsequently applied polymer. When the capillary was completely filled with the polymer solution, the open end was sealed by immersing it into silicone. Next the capillary filling nitrogen pressure was lowered to atmospheric pressure and left like this for 30 minutes to ensure a thorough sealing with the silicone. Subsequently, the other end was attached to a vacuum pump while the column was immersed into a temperature controlled water bath (40°C for poly(C_3Im^+ NTf_2^-) and 22°C for poly(ViC_4Im^+ NTf_2^-)). Now the vacuum was applied to evaporate the solvent resulting in the deposition of a thin layer of polymer onto the inner surface of the capillary. This procedure was completed within 48 hours for both polymer solutions.

2.6. Chromatographic conditions for GC

All analyses were performed on an Agilent 6890 GC-FID system with the exception of the FAME mix which was analysed on 7890B GC-FID system from the same manufacturer. Prior to chromatographic testing, the columns were subjected to various temperature ramps to compare the bleeding profiles from 40°C on at 2.5 °C/min up to 200°C, 250°C, 270°C, 300°C, 325°C and 350°C where the temperature was kept during 10 min before cooling the instrument. Hydrogen was used as a carrier gas throughout this work of which the flow rate was set at 1 ml/min in these initial experiments. All data points in the Van Deemter curves were collected in triplicate while the oven was set isothermally at 130°C. Exact column void times for the construction of the Van Deemter curve were obtained via injection of the headspace of dichloromethane (to avoid a saturated detector signal). During these and during the subsequent analyses 0.2 µL of sample was injected into a split/splitless liner with single taper, heated at 250°C, using a split ratio of 100:1. The flow rate of the carrier gas was set at 1.2 mL/min for the retention and selectivity study, corresponding to an average velocity of 40 cm/sec. Temperature gradients from 40°C to 200°C were thereby used at 2.5 °C/min. The linoleic acid methyl ester isomer mix was analysed using a temperature gradient from 60°C, held for 2 minutes, to 180°C at 8°C/min. 1 µl of the FAME mix was finally injected into a split/splitless liner with single taper, heated at 250°C, using a split ratio of 50:1. Separations were performed with hydrogen as carrier gas at a constant flowrate of 1.2 ml/min. Temperature gradients from 100°C, held for 1 minute, to 250°C were thereby used at 5 °C/min and held for 2 minutes. In all experiments the FID was operated at 250°C, with following gas flow settings: H_2 = 30 ml/min, Air = 300 ml/min; N_2 = 40 ml/min.

3. Results and discussion

3.1. Thermal properties of the (P)IL based columns

Although thermal gravimetric analysis doesn't necessarily reflect the applicability of a polymer as a coating in a gas chromatographic column, it allows comparison of the relative stability of materials. The thermograms of both types of polymer with various counterions are represented in Figure 4. With chloride containing polymers an initial weight loss is observed below 100°C. This is related to the hygroscopic nature of these polymers. When exchanging the chloride or bromide counterions with bis(trifluoromethane)sulfonimide, an increase in thermal stability of over 100°C is observed confirming the significant stabilizing effect this group offers [32]. Comparison of the condensation type polymer with the one obtained via free radical polymerisation learns that the former depicts significantly improved thermal stability compared to the latter as observable degradation via TGA is only measured from 400°C on for poly(C_3Im^+ NTf_2^-) compared to 300°C for poly(ViC_4Im^+ NTf_2^-). Note that the inorganic residue of poly(C_3Im^+ NTf_2^-) is about 5% higher compared to poly(ViC_4Im^+ NTf_2^-). This is a consequence of the larger relative weight of the counterion in the former polymer.

Figure 4

287 Evaluation of the influence of the thermal properties of the polymers on the applicability in gas
288 chromatography is only possible via direct evaluation of the columns in GC as a minor weight loss in a
289 TGA experiment can already result in saturated background signals, losses in retention time and peak
290 symmetry limiting the practical relevance of columns coated with such polymers. Therefore the
291 bleeding profile of the columns coated with both polymers were measured and compared with a
292 commercial SLB-IL111 column in GC-FID as shown in Figure 5. Both in-house made columns were
293 therefore ramped up (at 2.5°C/min) to 200°C, 250°C, 270°C, 300°C and additionally to 325°C and
294 350°C for poly(C_3Im^+ NTf_2^-). The commercial SLB-IL111 was used up to its maximum allowable
295 operating temperature (MAOT) of 270°C where the increase in background signal measured 20 pA
296 (Figure 5C). When increasing the temperature up to 300°C, the degradation of this phase resulted in
297 an excessive bleeding signal of more than 100 pA. When comparing this data to the performance of
298 both polymeric ionic liquid phases significant disparities appeared between the polymer obtained by
299 free radical polymerization and the one synthesized via the condensation reaction. The former
300 poly($ViC_4Im^+NTf_2^-$) already depicted a significant bleeding profile below 250°C and therefore
301 underperformed compared to the commercial (non-polymeric) ionic liquid based column. Further
302 heating to 300°C let to intense degradation of the stationary phase. This pattern was not unexpected
303 at it corroborates the TGA data. By contrast it has been reported that the similar (yet not equal)
304 poly(1-vinyl-3-hexylimidazolium) polymer (containing a hexyl instead of the butyl group used in this
305 work) depicted onset bleed temperatures of 335°C-345°C [36]. The latter data was, however,
306 obtained on shorter columns (5 m) coated with thinner films (as calculated with equation 1). As can
307 be seen in Figure 5 the bleeding observed in the columns coated with the polymer obtained the step
308 growth mechanism poly(C_3Im^+ NTf_2^-) appeared significantly lower compared to the other two
309 columns.

310 When increasing the maximum temperature of the temperature gradient to 325°C for this polymer, a
311 comparably yet slightly higher bleeding of 30 pA was obtained as measured at the maximal operating
312 temperature for the of SLB-IL111 at 270°C. Increasing the maximum temperature for this polymer up
313 to 350°C resulted in a bleeding profile that was in the same range as when SLB-IL111 was heated
314 above its maximum operating temperature to 300°C. As the commercial column is characterized by
315 at thinner film thickness of 0.20 μm compared to 0.25 μm for the poly(C_3Im^+ NTf_2^-) based column this
316 data illustrates the practical potential of the latter polymer as coating material in GC for the analysis
317 of very polar solutes in terms of thermal stability. Note that when heating the poly(C_3Im^+ NTf_2^-) based
318 column to 350°C, subsequently no loss of column performance was measured neither in plates or
319 retention. This is, however, obviously bound to be detrimentally affected upon long exposure of this
320 polymer to such temperatures. Although the improved stability of the condensation type polymer is
321 apparent it is surprising that it has thus far been the lesser described and used type in terms of
322 imidazolium based GC columns. To the best of our knowledge the description of the use of the
323 condensation type of polymer in GC has been limited to one contribution [39]. Unfortunately in
324 literature few chromatograms can be found obtained on this type of stationary phase, whereby
325 analysis is limited to apolar solutes, alcohols and phthalates complicating assessment of the relative
326 performance of columns coated with the chain and step growth polymerization, respectively.

327 **Figure 5**

328 ## 3.2.   Column efficiency study
329 In order to determine the optimal operation conditions of the manufactured columns and to obtain
330 more insight into mass transfer aspects of this type of stationary phases, the corresponding Van
331 Deemter curves were constructed via isothermal GC-FID experiments [5]. The lowest plate heights
332 while still retaining sufficient retention to assess the latter without distortion were obtained at

333   130°C. The corresponding plots for benzaldehyde, acetophenone, 1-methylnaphthalene and aniline
334   on both developed column types and a commercial SLB-IL111 column are depicted in Figure 6.
335   Representative chromatograms are provided in the supplementary information section. In general,
336   the commercial IL column provided somewhat lower plate-heights compared to both PIL columns,
337   while both in-house made columns resulted in very similar Van Deemter curves. For the majority of
338   the data points relative standard deviations on measured plate heights were below 5%, with some
339   transgressions thereof in the B term regime where analysis times are long and peaks are much
340   broader typically leading to somewhat poorer precision. As can be seen in Figure 6 and as depicted in
341   Table 1 on the commercial column, minimal plate heights reached 0.3 mm at optimal velocities
342   varying between 41 and 62 cm/sec. On the column coated with the condensation type polymer, the
343   plate heights ranged between 0.394 and 0.479 mm with corresponding optimal velocities between
344   31 and 44 cm/sec. The columns coated with the PIL obtained via free radical polymerisation led to
345   somewhat higher minimal plate heights varying between 0.433 and 0.514 mm with comparable
346   optimal velocities as observed for the other PIL phase. Towards small polar molecules that depict no
347   protic interaction with the stationary phase, like acetophenone the Van Deemter curves obtained on
348   both PIL columns appeared similar, while approaching the performance of a commercial ionic liquid
349   column. For protic analytes like aniline a somewhat larger deviation from the optimal plate heights
350   seems to occur. The columns made in this work consequently allowed reaching 2000-2500 plates/m
351   for the various solutes with retention factors between 0.77 and 3.05. Although this is 40-50% less
352   compared to the theoretically expected 4000 plates/m achievable on thin film PDMS columns, the
353   obtained data compares favourably with literature [37] as the data was obtained for both PILs on
354   conventional column dimension (30 m x 0.25 mm) and film thicknesses (0.25 µm) facilitating
355   subsequent practical implementation. Note that although higher plate counts can be obtained when
356   further raising the temperature, this inevitably leads to significant reductions in retention and to
357   artificially enhanced plate counts due to the reduced residence time in the stationary phase. As
358   retention factors are quite low in these experiments, benzylbenzoate (k = 17.98 for poly(ViC$_4$Im$^+$NTf$_2^-$
359   ) and k = 20.62 for poly(C$_3$Im$^+$ NTf$_2^-$)) was injected, resulting in comparable plate heights to those
360   obtained with the 4 analytes. The C term appears somewhat steeper in the polymerized phases, this
361   appears to be related to the slower diffusion in stationary phase although it cannot be excluded that
362   this could also be caused by coating imperfections or wettability issues as it was observed that the
363   application of straightforward column pre-treatment procedures (see experimental section)
364   significantly improved the measured columns efficiencies. Interestingly the mass transfer in both
365   polymerized stationary phases appears not excessive compared to the non-polymerized ionic liquid
366   column illustrating the non-trivial fact that diffusion in a polymerized stationary phase of this type is
367   not significantly affected by polymerization process. Also it should be noted that obtaining
368   comparable, usable plate heights of between 0.4 and 0.5 mm on both types of polymer is of
369   relevance as one might have expected that the polymer depicting higher imidazolium density
370   obtained via condensation polymerisation could have led to slower mass transfer. As in all
371   experiments the column efficiencies obtained on the column coated with the condensation type
372   polymer outperforms slightly the columns coated to the chain growth polymer, while the former also
373   depicts the higher thermal stability this strengthens the case for more broader usage of the
374   condensation type of imidazolium based column coating, which has as mentioned thus far been
375   somewhat neglected to the benefit of the broader use of the chain growth polymers. Note again that
376   in the current work the alkyl side chain on the PIL obtained via free radical polymerisation is shorter
377   compared to previous studies [36,37].

378   **Figure 6**

379   **Table 1**

3.3.   Retention and selectivity evaluation of the PIL phases

In order to obtain a broader idea on the relative retention, selectivity and peak symmetry characteristics of the prepared PIL columns, a mixture of 8 compounds possessing different functionalities was injected on the PIL based columns (Figure **7**). Aniline (E) appears significantly more retained on the poly(C_3Im$^+$ NTf$_2^-$) based column, while carvone (C) and γ-nonanoic lactone (G) were more retained on poly(ViC$_4$Im$^+$NTf$_2^-$) based phases. For the other compounds comparable retention times are observed. The increased retention of bases such as aniline reflects increased protic and dipole-dipole interactions of the condensation based polymer compared to the chain growth based polymers. This can be related to improved accessibility of the imidazolium-groups in poly(C_3Im$^+$ NTf$_2^-$). The increased retention of the (non-aromatic) carvone (C) and γ-nonanoic lactone (G) could be related to the hydrophobic interactions with the aliphatic carbon chain poly(ViC$_4$Im$^+$ NTf$_2^-$). Overall the peak shape of all solutes appeared better on poly(C_3Im$^+$ NTf$_2^-$) compared to poly(ViC$_4$Im$^+$ NTf$_2^-$), confirming the higher plate counts which were achieved on the former column. Also note the rising background in the chromatogram of poly(ViC$_4$Im$^+$NTf$_2^-$), whereas the baseline of the more thermally stable poly(C_3Im$^+$ NTf$_2^-$) is unaffected, confirming the prior bleeding tests.

Figure 7

Rationalisation of the qualitative assessment above can be obtained via measurement of the retention indices. In this way, one can compare several stationary phases towards their affinity with certain functional groups in organic molecules. 7 molecules, containing no hetero-atoms as well as an alkane series (C_7-C_{17} + C_{22}) were therefore injected and their respective Kovats indices were calculated, represented in Table 2. This largely apolar mixture was selected as it has been extensively used for column selectivity assessment before and shows relevance to depict the capacity of the column to separate the aromatic from the aliphatic solutes. It is clear that for all compounds in this mixture, the retention index is the highest using the commercial ionic liquid column, while the condensation polymer resulted in the lowest ones, except for mesitylene and 1-methylnaphthalene. The structure of poly(C_3Im$^+$NTf$_2^-$) where there is the lesser availability of alkyl chains seems to result in an overall lower affinity towards alkanes. The bi-aromatic solute is more retained on this phase possibly due to the better accessibility allowing more aromatic interactions. The aromatic retention is not reflected with tri-t-butylbenzene, probably due to the steric interactions depicted by this molecule.

Table 2

As ionic liquid based columns show most promise and relevance for the analysis of polar solutes, comparison of the McReynolds constants for the respective columns can provide more insight into the merits of the developed columns. The procedure involved injection of 5 polar solutes whereby retention indices are compared to the ones obtained on a non-polar squalane based column [42]. Based on these values interactions such as dispersion, dipole and proton acceptor/donor can be identified. The five resulting McReynolds constants for all 4 columns can be seen in Table 3. The overall polarity of the condensation polymer appears similar to that of SLB-IL111, while poly(ViC$_4$Im$^+$ NTf$_2^-$) is significantly less polar. Towards aromatic structures such as benzene, the condensation based polymer showed significant affinity, confirming the above observed retention of non-sterically hindered aromatic solutes. The polar retention of the alcohols and ketones containing compounds appeared similar between the poly(C_3Im$^+$ NTf$_2^-$) based column and the commercial analogue. Towards nitropropane, the McReynolds constant of poly(C_3Im$^+$ NTf$_2^-$) somewhat lower than for SLB-IL111. Both polymers are characterized by a significant degree of protic interactions as the McReynolds constant for pyridine is considerable larger compared to the one for the ionic liquid column.

425 The data can be summarized as followed: for the chain-growth polymer interactions are comparable
426 to those measured on a WAX column, with exception for pyridine, for which the proton
427 donor/acceptor capabilities are much higher. The condensation polymer based column shows
428 similarity with some of the most polar commercially available ionic liquid columns, while possessing
429 additional proton donor capacities.

430 **Table 3**

431 In order to illustrate the potential of the poly($C_3Im^+NTf_2^-$) based column a number of selected group
432 type application is shown in Figure 8. A comparison was thereby made with the poly($ViC_4Im^+NTf_2^-$)
433 based column. Overall it appeared that solutes containing carbonyl or ester functionalities retain
434 particularly well and with excellent peak symmetries on the poly($C_3Im^+NTf_2^-$) based column. On both
435 columns separation and peak shapes were good for the phenone series, with symmetry factors of 0.8
436 to 1.2. Again note the difference in rising of the background between both stationary phases, as the
437 condensation polymer showed virtually no increase, whereas poly($ViC_4Im^+NTf_2^-$) showed some
438 considerable background while eluting hexanophenone.

439 **Figure 8**

440 ## 3.4.   Case study: Separation of 37 fatty acid methyl esters

441 Commercial ionic liquid columns like SLB-IL111 have frequently been applied for the separation of
442 fatty acid methyl esters (FAMEs) [43,44]. As the condensation polymer showed a similar polarity to
443 this commercial column, a 37 component FAME mix was analysed, depicted in Figure 9A. Identity of
444 the compounds was confirmed using GC-MS. Since the poly($C_3Im^+NTf_2^-$) column was only 30 meters
445 long, no complete separation of all compounds was achieved. Separation was insufficient for the
446 cis/trans isomer of C18:1n9, for the positional isomers of C20:3 and for mono-unsaturated versus
447 saturated higher fatty acids methyl esters (C22 and C24). All other analytes showed good peak
448 symmetry. It should be noted that compared to the separation with the commercial column, some
449 elution differences were observed. For example C15:1 eluted after C16 on the SLB-IL111 stationary
450 phase, while this is not the case for the condensation polymer. To show the capabilities of the
451 condensation polymer towards the separation of cis/trans isomers, a mixture containing 4 cis/trans
452 isomers of linoleic acid was injected, shown in Figure 9B. It is observed that separation is achieved
453 despite the lack of plates using this column.

454 **Figure 9**

455 # 4.   Conclusion

456 A one to one comparison between gas chromatographic columns coated with imidazolium based
457 polymerized ionic liquid obtained via a step and chain growth mechanism is performed in this work.
458 A superior performance of the condensation type polymer is thereby observed compared to the one
459 obtained via a free radical polymerization mechanism in terms of thermal stability, columns
460 efficiency, minimal plate heights, retention of polar solutes and the peak shape thereof. Although
461 higher plate heights are still obtained compared to commercial non polymerized ionic liquid based
462 columns, it appears that the polymerisation thereof does not lead to significant reductions in
463 diffusivity in the stationary phase and in this way does not hinders the chromatographic potential,
464 while increasing the thermal stability of the material. The late onset of significant column bleeding at
465 325°C of the column coated with the condensation type of polymer when using
466 bis(trifluoromethane)sulfonimide as counterion broadens the applicability range of this type of
467 columns. The PIL based columns depict interesting selectivities towards amine, carbonyl and ester

468 functionalities with excellent peak shapes, while showing promising separation potential for the
469 analysis of fatty acid methyl esters.

470

Acknowledgements

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Figure Captions

Figure 1: Structure of 2 commercial ionic liquid GC stationary phases (n = 1: SLB-IL111; n = 8: SLB-IL82) (A) and two polymeric ionic liquids applied as stationary phase in GC in this study. Poly(1-vinyl-3-alkylimidazolium X⁻), obtained via a chain-growth polymerization (B) and poly(propylimidazolium X⁻), synthesized using a step-growth mechanism.

Figure 2: Synthesis of 3-chloropropylimidazole, followed by the step-growth polymerization towards Poly(propylimidazolium – chloride) (poly(C_3Im^+ Cl^-)) and ion exchange to obtain the final polymer: Poly(propylimidazolium – bis(trifluoromethane)sulfonimide) (poly(C_3Im^+ NTf_2^-)).

Figure 3: Synthesis of 1-vinyl-3-butylimidazolium bromide, followed by the chain-growth polymerization to obtain Poly(1-vinyl-3-butylimidazolium bromide) (poly(ViC_4Im^+ Br^-)) and ion exchange to form the final polymer: Poly(1-vinyl-3-butylimidazolium - bis(trifluoromethane)sulfonimide) (poly(ViC_4Im^+ NTf_2^-))

Figure 4: Thermal gravimetric analysis of the poly(C_3Im^+ X^-) and poly(ViC_4Im^+ X^-) with X being Cl^-/Br^- or NTf_2^-. Temperature program: 25°C-800°C at a heating rate of 10°C/min; N_2 flow: 200 ml/min.

Figure 5: Bleeding profiles of prepared PIL columns and commercial SLB-IL111 column for a blank analysis on GC-FID with a temperature program starting at 40°C and ending at different temperatures for 10 minutes (A = 200°C, B = 250°C, C = 270°C, D = 300°C, E = 325°C, F = 350°C).

Figure 6: Constructed Van Deemter curves for 2 in-house made PIL columns (poly(C_3Im^+ NTf_2^-)(●); poly(ViC_4Im^+ NTf_2^-)(Δ)) and a commercial IL column (x) for 4 molecules (A = Benzaldehyde, B = Acetophenone, C = 1-methylnaphthalene and D = Aniline). Oven temperature: 130°C

Figure 7: Analysis of 8 compounds on GC columns with poly(C_3Im^+ NTf_2^-) and poly(ViC_4Im^+ NTf_2^-) as stationary phase (30m x 0.25 mm x 0.25 μm; oven temperature: 40°C - 200°C @ 2.5°C/min, H_2 flow: 1.2 ml/min (A = Benzaldehyde; B = Methylsalicylate; C = Carvone; D = 3-nitrotoluene; E = Aniline; F = Cinnamaldehyde; G = γ-nonanoic lactone; H = Benzylbenzoate)

Figure 8: Analysis of 4 phenones and of benzylacetate on GC columns with poly(C_3Im^+ NTf_2^-) and poly($ViC_4Im^+$$NTf_2^-$) as stationary phase (30m x 0.25 mm x 0.25 μm; oven temperature: 40°C - 200°C @ 2.5°C/min, H_2 flow: 1.2 ml/min (A = Acetophenone; B = Propiophenone; C = Butyrophenone; D = Benzylacetate; E = Hexanophenone)

Figure 9: A: Analysis of 37 component FAME mix using poly(C_3Im^+ NTf_2^-) as stationary phase (30m x 0.25 mm x 0.25 μm; oven temperature: 100°C (1 min) - 250°C @ 5°C/min, hold 2 min), H_2 flow: 1.2 ml/min (1 = C4:0; 2 = C6:0; 3 = C8:0; 4 = C10:0; 5 = C11:0; 6 = C12:0; 7 = C13:0; 8 = C14:0; 9 = C14:1; 10 = C15:0; 11 = C15:1; 12 = C16:0; 13 = C16:1; 14 = C17:0; 15 = C17:1; 16 = C18:0; 17 = C18:1n9c; 18 = C18:1n9t; 19 = C18:2n6c; 20 = C18:2n6t; 21 = C18:3n6; 22 = C18:3n3; 23 = C20:0; 24 = C20:1n9; 25 = C20:2; 26 = C20:3n6; 27 = C20:3n3; 28 = C20:4n6; 29 = C20:5n3; 30 = C21:0; 31 = C22:0; 32 = C22:1n9; 33 = C22:2; 34 = C22:6n3; 35 = C23:0; 36 = C24:0; 37 = C24:1n9); B: Analysis of linoleic acid methyl ester isomer mix using poly(C_3Im^+ NTf_2^-) as stationary phase (30m x 0.25 mm x 0.25 μm; oven temperature: 60°C (2 min) - 200°C @ 8°C/min), H_2 flow: 1.2 ml/min (1 = C18:2n9t, 12t; 2 and 3 = C18:2n9c, 12t andC18:2n9t, 12c; 4 = C18:2n9c, 12c)

SLB-IL111	Benzaldehyde	Acetophenone	1-Methylnaphthalene	Aniline
H_{opt} (mm)	0.298	0.303	0.303	0.302
U_{opt} (cm/sec)	61.65	61.65	56.49	40.86
k	1.09	2.08	3.69	3.30

poly($C_3Im^+NTf_2^-$)	Benzaldehyde	Acetophenone	1-Methylnaphthalene	Aniline
H_{opt} (mm)	0.394	0.436	0.479	0.441
U_{opt} (cm/sec)	39.65	39.65	30.58	44.13
k	0.77	1.44	1.83	3.05

poly($ViC_4Im^+NTf_2^-$)	Benzaldehyde	Acetophenone	1-Methylnaphthalene	Aniline
H_{opt} (mm)	0.441	0.433	0.488	0.514
U_{opt} (cm/sec)	31.87	41.39	31.87	41.39
k	0.80	1.01	1.08	1.09

Table 1: Overview of the optimal plate heights, velocities and retention factors for 4 compounds (Benzaldehyde, Acetophenone, 1-methylnaphthalene and Aniline) on the commercial SLB-IL111 column and 2 in house manufactured PIL columns (poly($C_3Im^+NTf_2^-$) and poly($ViC_4Im^+NTf_2^-$)).

Molecule	poly($C_3Im^+ NTf_2^-$)	poly($ViC_4Im^+ NTf_2^-$)	SLB-IL111
Butylcyclohexane	1008.3	1056.9	1099.9
Decalin trans	1065.8	1112.4	1199.2
Decalin cis	1107.4	1162.6	1262.2
Mesitylene	1339.8	1182.5	1432.1
Bicyclohexyl	1257.6	1360.6	1521.7
Tri-t-butylbenzene	1454.8	1536.7	1633.2
1-methylnaphthalene	2052.6	1775.3	2449.4

Table 2: Kovats indices of 7 organic molecules on two in house made PIL columns (poly($C_3Im^+ NTf_2^-$) and poly($ViC_4Im^+ NTf_2^-$)) and a commercial SLB-IL111 column.

Probe compound	poly(C$_3$Im$^+$NTf$_2^-$)	poly(ViC$_4$Im$^+$NTf$_2^-$)	SLB-IL111	DB-WAX
Benzene	521	223	553	283
1-butanol	771	594	823	580
2-pentanone	617	360	655	289
Nitropropane	818	598	931	523
Pyridine	1016	1064	853	454
Sum	3743	2839	3815	2130

693 **Table 3: McReynolds constants for 5 probe molecules on two in house made PIL columns ((poly(C$_3$Im$^+$ NTf$_2^-$) and**
694 **poly(ViC$_4$Im$^+$ NTf$_2^-$)), a commercial SLB-IL111 and DB-WAX column.**

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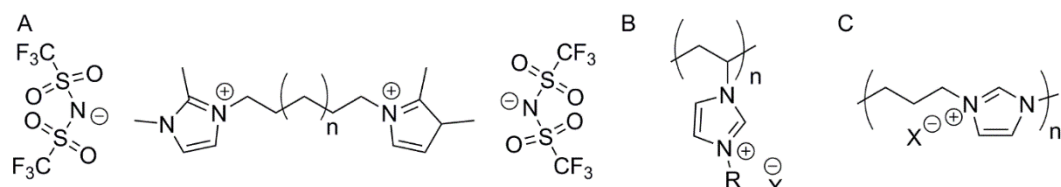
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720   **Figure 1**

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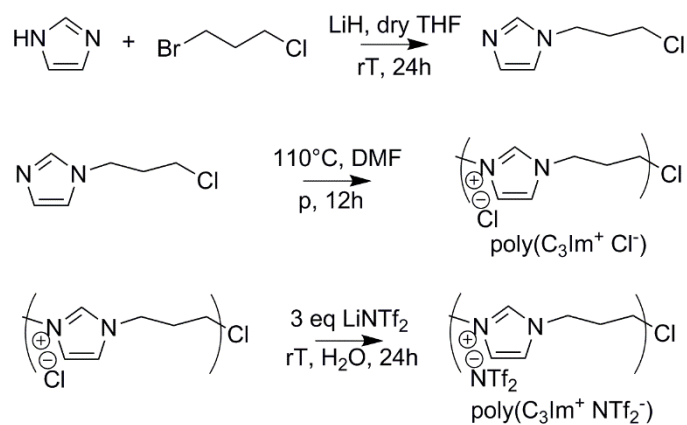
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725   **Figure 2**

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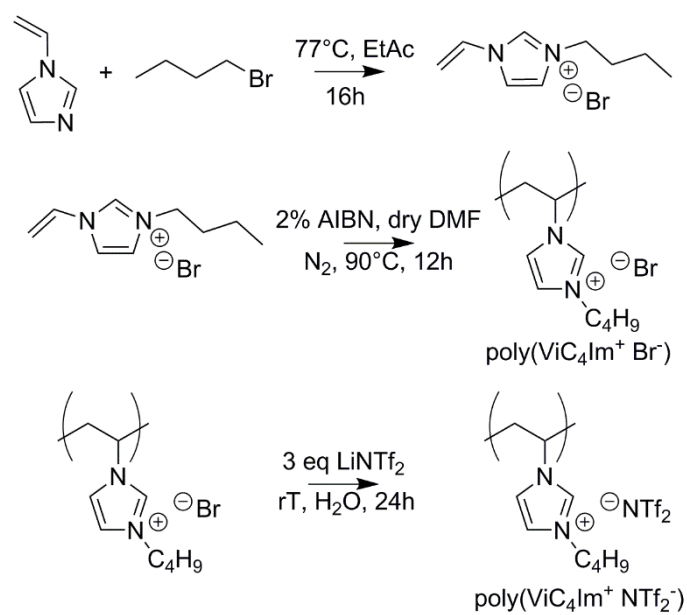
728

729   **Figure 3**

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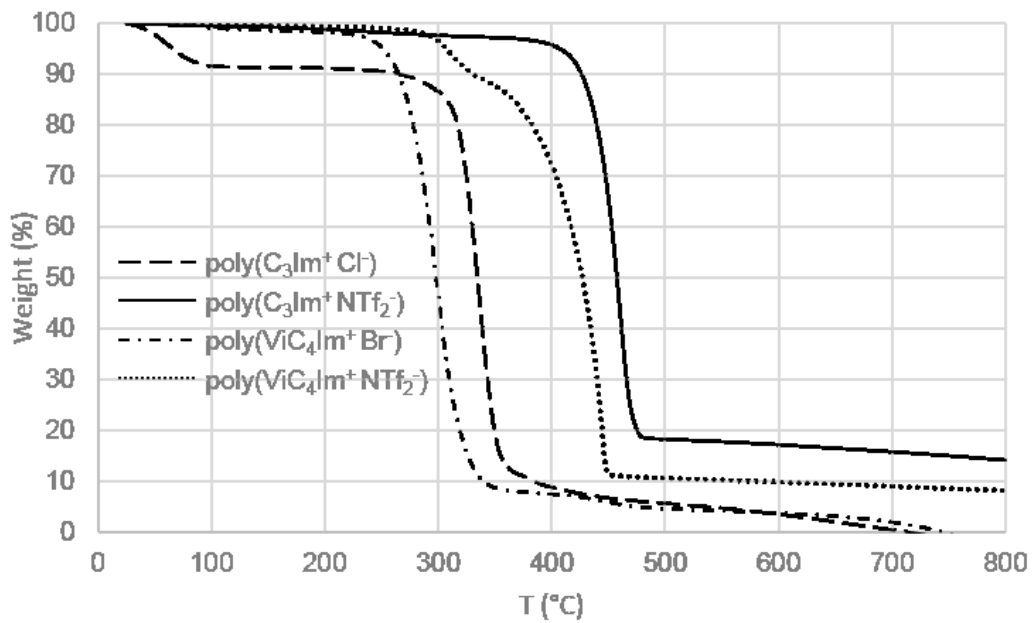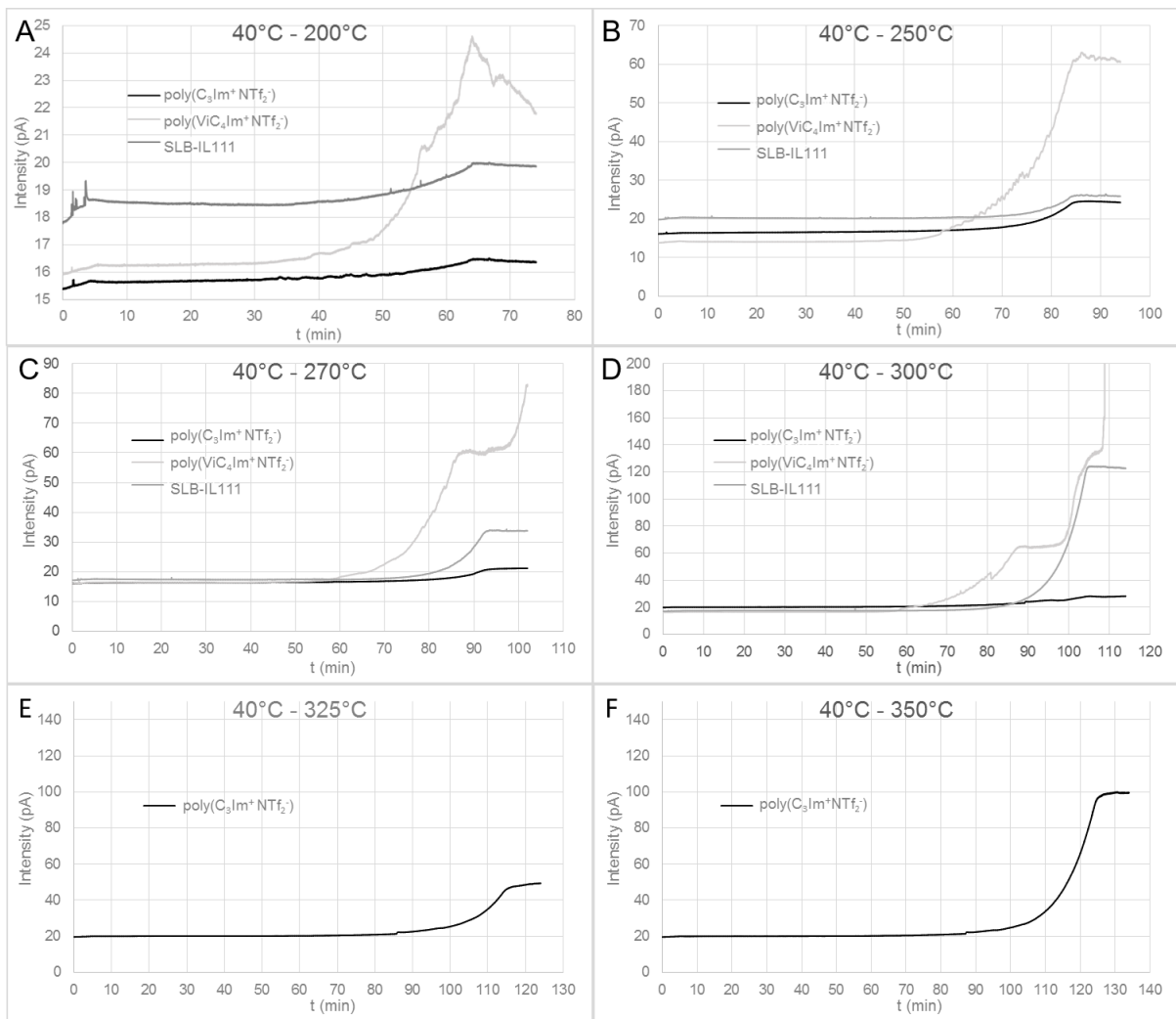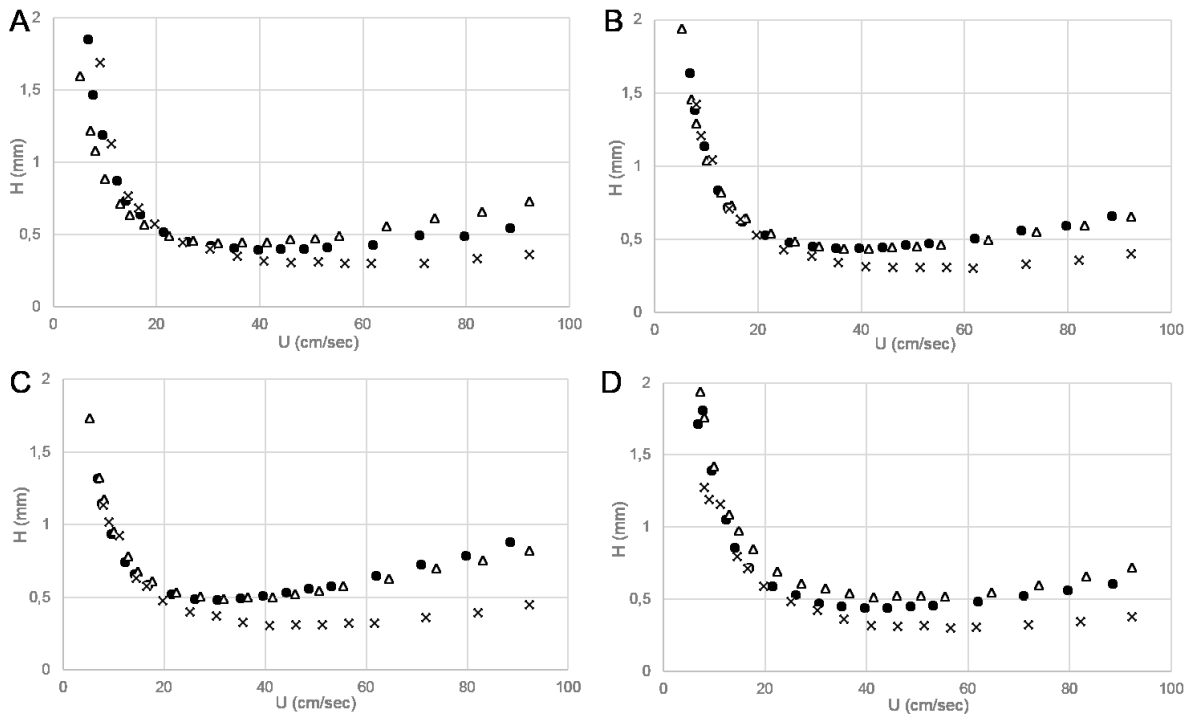
731

Figure 4

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737   **Figure 5**

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Figure 6

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759 **Figure 7**

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762 **Figure 8**

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766 **Figure 9**
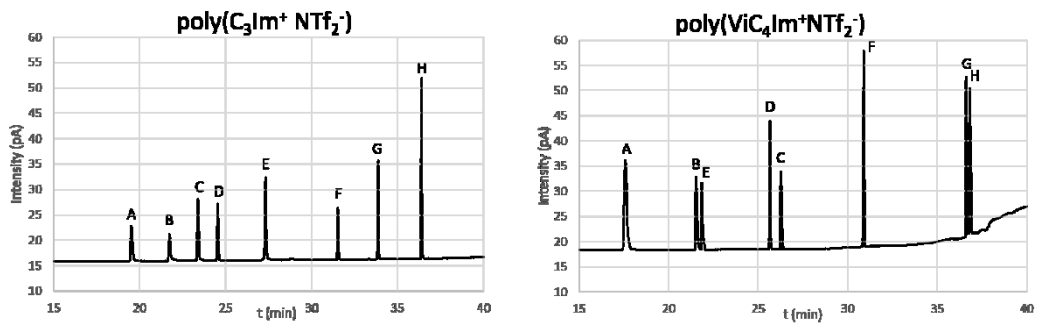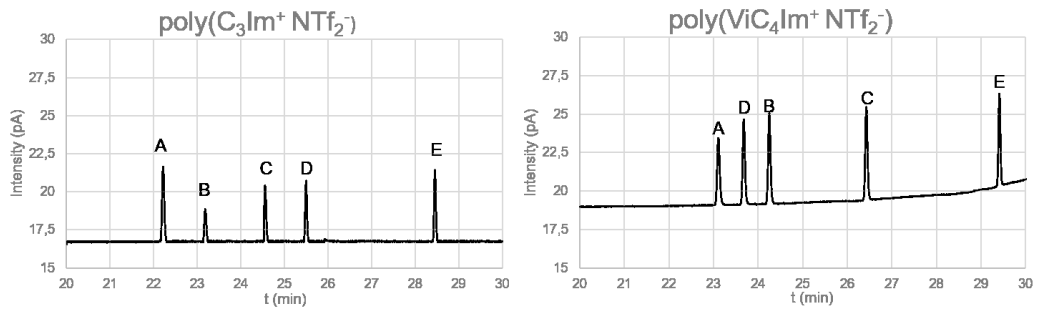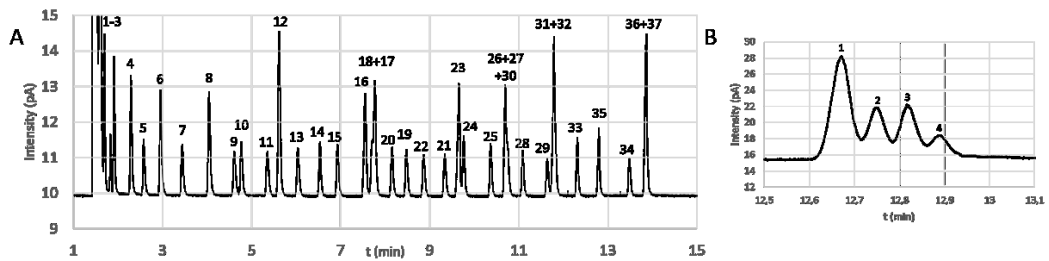
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Article supplementary information

NMR Data

1-(3-chloropropyl)-1H-imidazole

^{1}H NMR (400 MHz, DMSO): 7.64 (1H), 7.19 (1H), 6.90 (1H), 4.09 (2H), 3.54 (2H), 2.16 (2H)
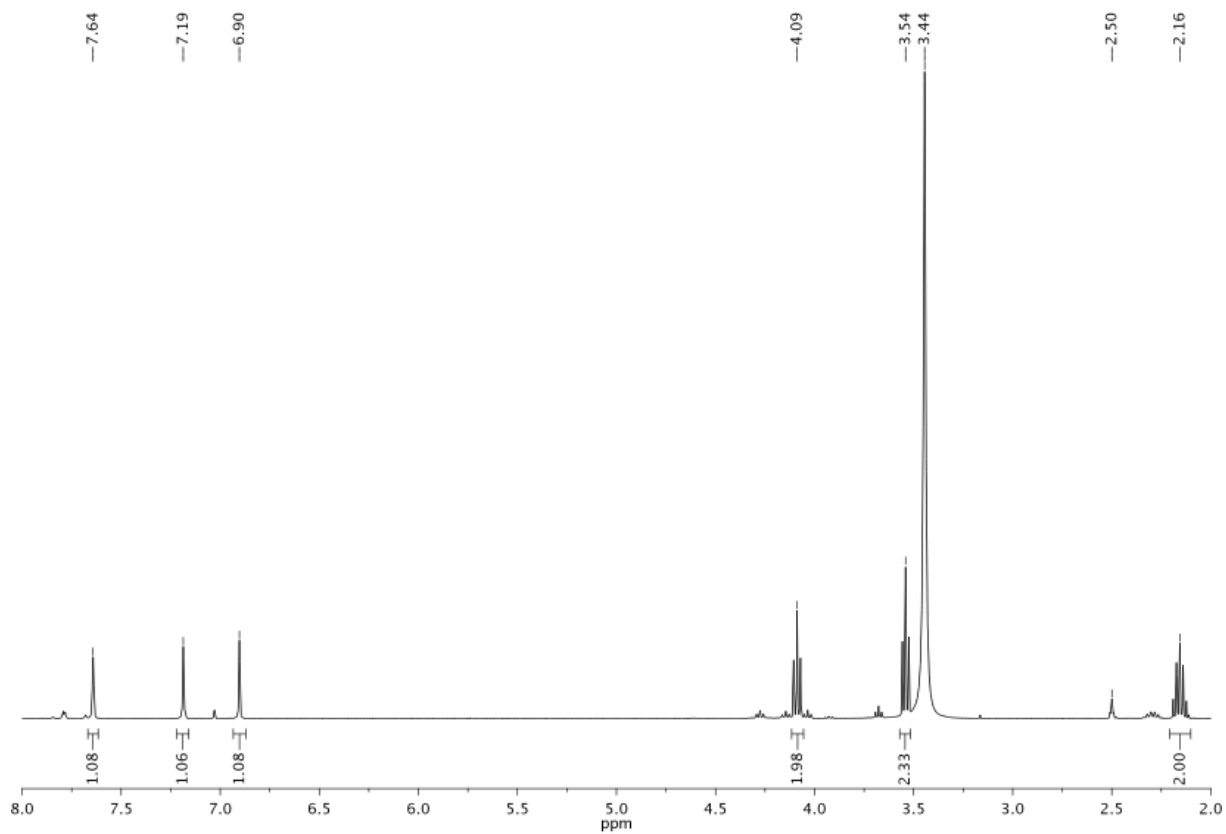
792 **1-vinyl-3-butyl-imidazolium chloride (ViC$_4$Im$^+$ Cl$^-$)**

793 ^{1}H NMR (400 MHz, D$_2$O): 9.09 (1H), 7.81 (1H), 7.63 (1H), 7.18 (1H), 5.86 (1H), 5.47 (1H), 4.29 (2H),
794 1.92 (2H), 1.37 (2H), 0.96 (3H)

795
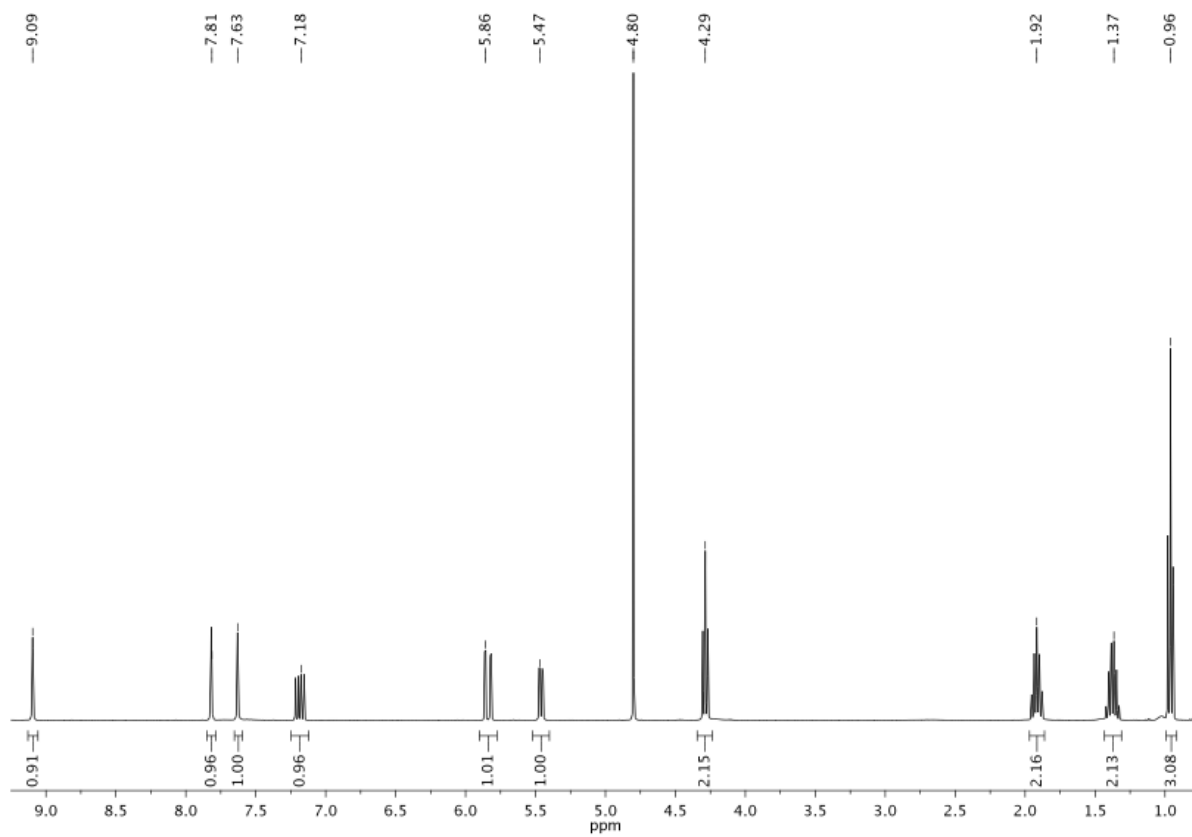
796
797

798 **Poly(C₃Im⁺ Cl⁻)**

799 ^{1}H NMR (400 MHz, D$_2$O): 9.02 (1H), 7.63 (2H), 4.39 (4H), 2.58 (2H)

800
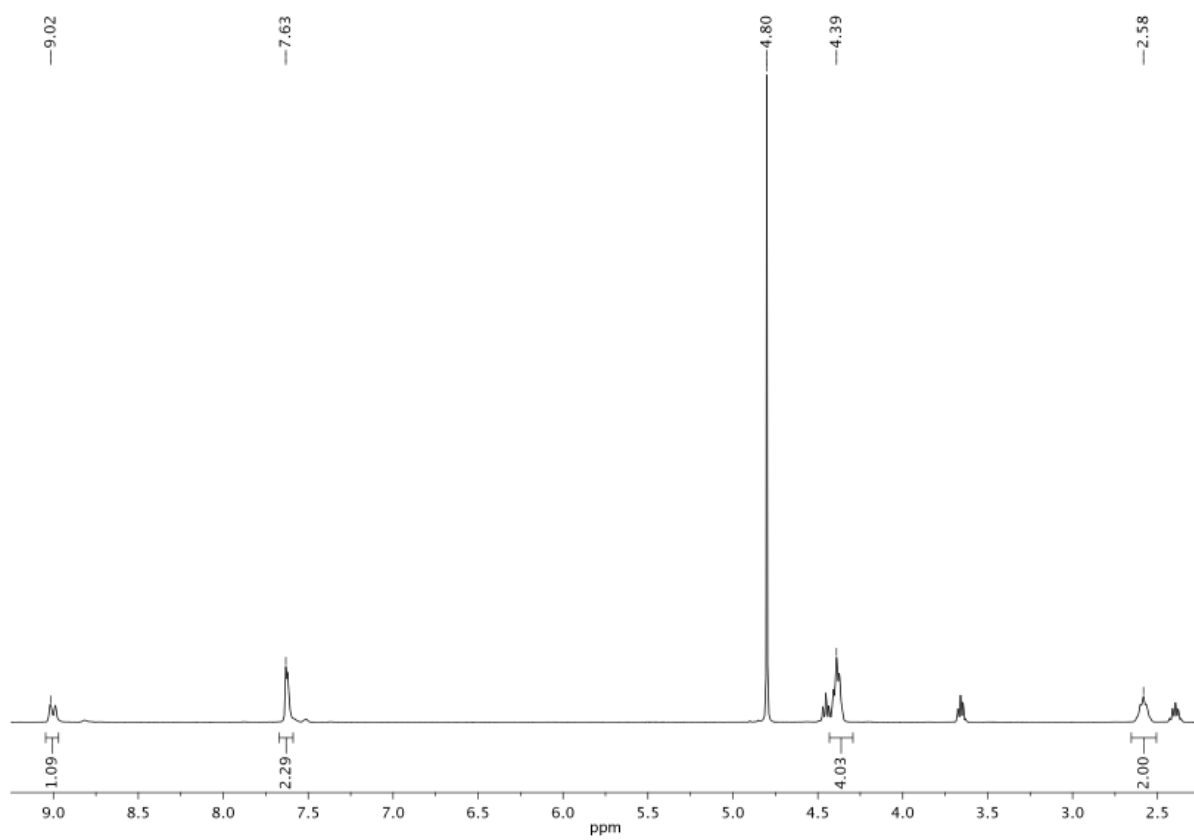
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804 **Poly(ViC₄Im⁺ Cl⁻)**

805 ¹H NMR (400 MHz, D₂O): 7.55 (2H), 4.85 (1H), 4.53-4.16 (3H), 2.58 (2H), 1.86 (2H), 1.40 (2H), 0.99
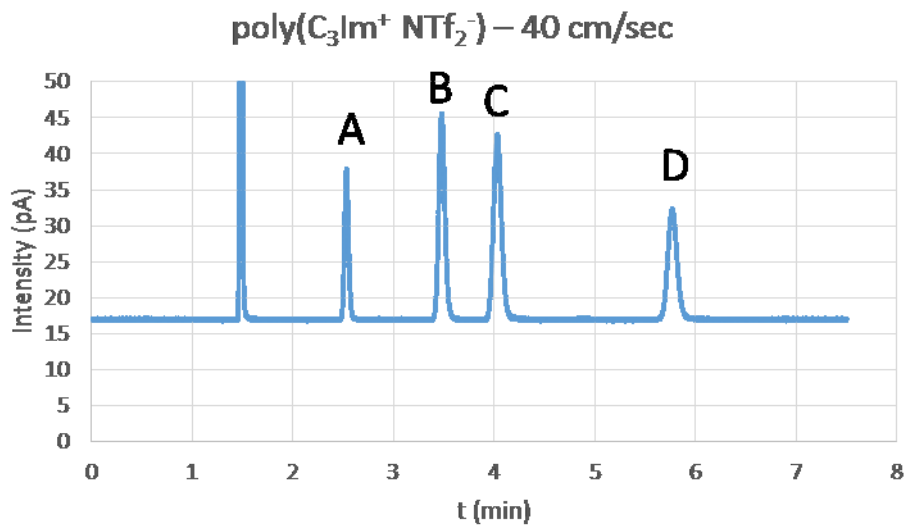806 (3H)
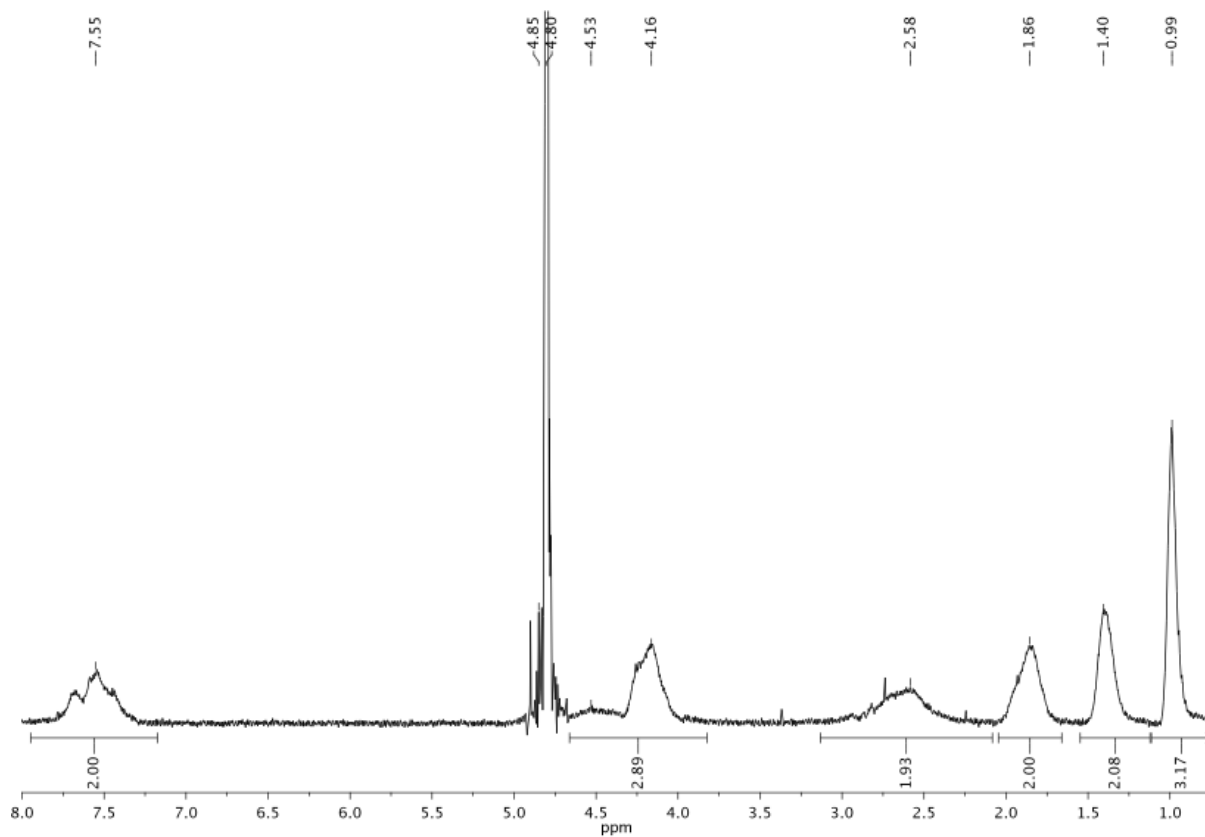
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815   Representative chromatogram Van Deemter

816   2.7.   poly($C_3Im^+ NTf_2^-$)
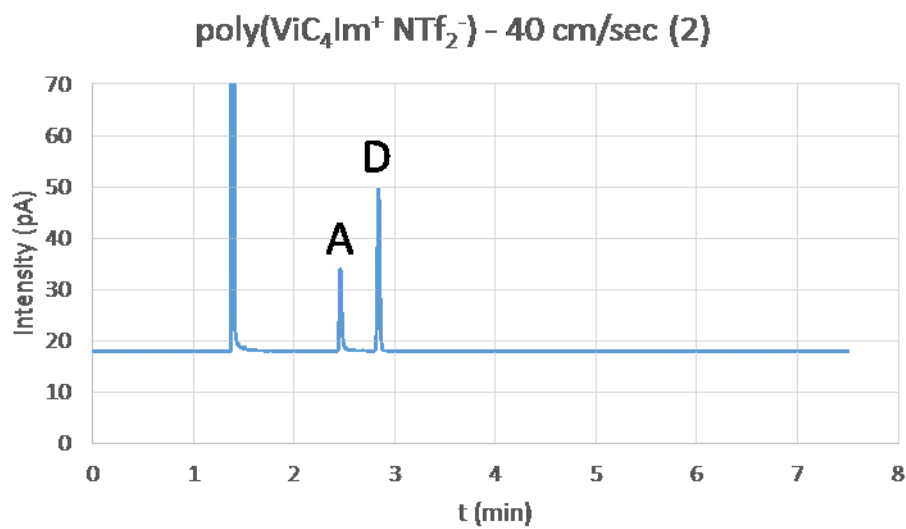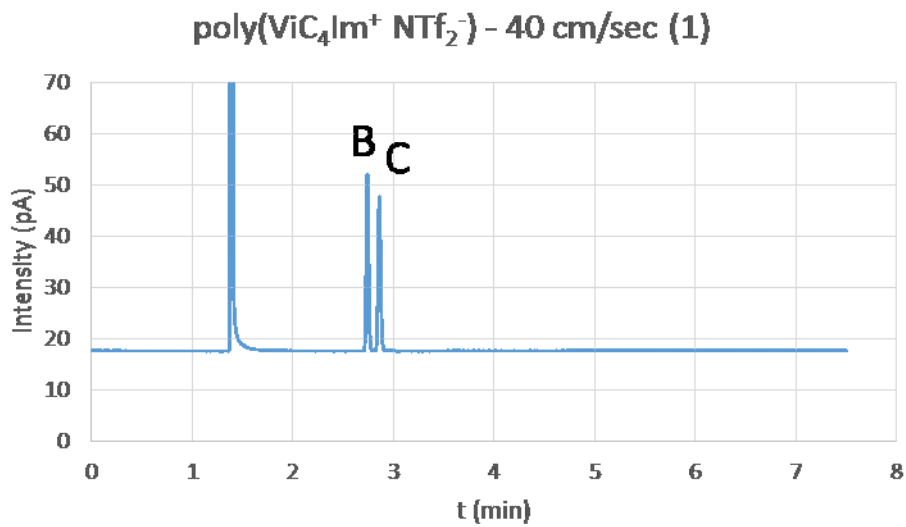
817   2.8.   40 cm/sec

poly($C_3Im^+ NTf_2^-$) – 40 cm/sec

818

819   A = Benzaldehyde; B = Acetophenone; C = 1-methylnaphthalene; D = Aniline

820

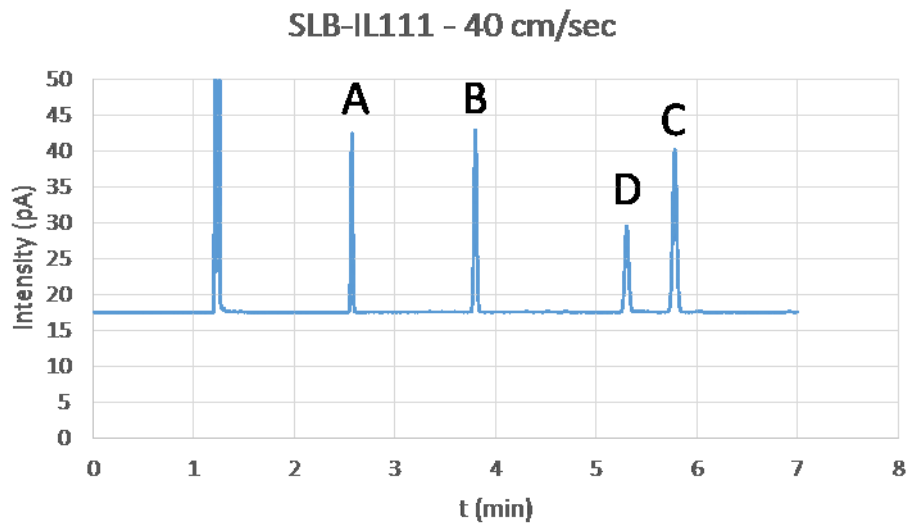821   2.9.   poly(ViC$_4$Im$^+$ NTf$_2^-$)

822   2.10.   40 cm/sec

poly(ViC$_4$Im$^+$ NTf$_2^-$) – 40 cm/sec (1)

poly(ViC$_4$Im$^+$ NTf$_2^-$) – 40 cm/sec (2)

823

824   A = Benzaldehyde; B = Acetophenone; C = 1-methylnaphthalene; D = Aniline

825

826   2.11.   SLB-IL111

827   2.12.   40 cm/sec

SLB-IL111 – 40 cm/sec

828

829   A = Benzaldehyde; B = Acetophenone; C = 1-methylnaphthalene; D = Aniline

830

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