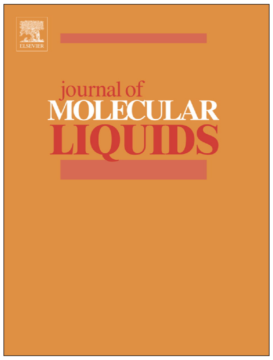

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Synthesis and characterization of potentially polymerizable amine-derived ionic liquids bearing 4-vinylbenzyl group

Adrian Zajac,[1]* Andrea Szpecht,[1,2] Dawid Zielinski,[1] Krzysztof Rola,[3] Jakub Hoppe,[1,2] Katarzyna Komorowska,[3,4] Marcin Smiglak[1]*

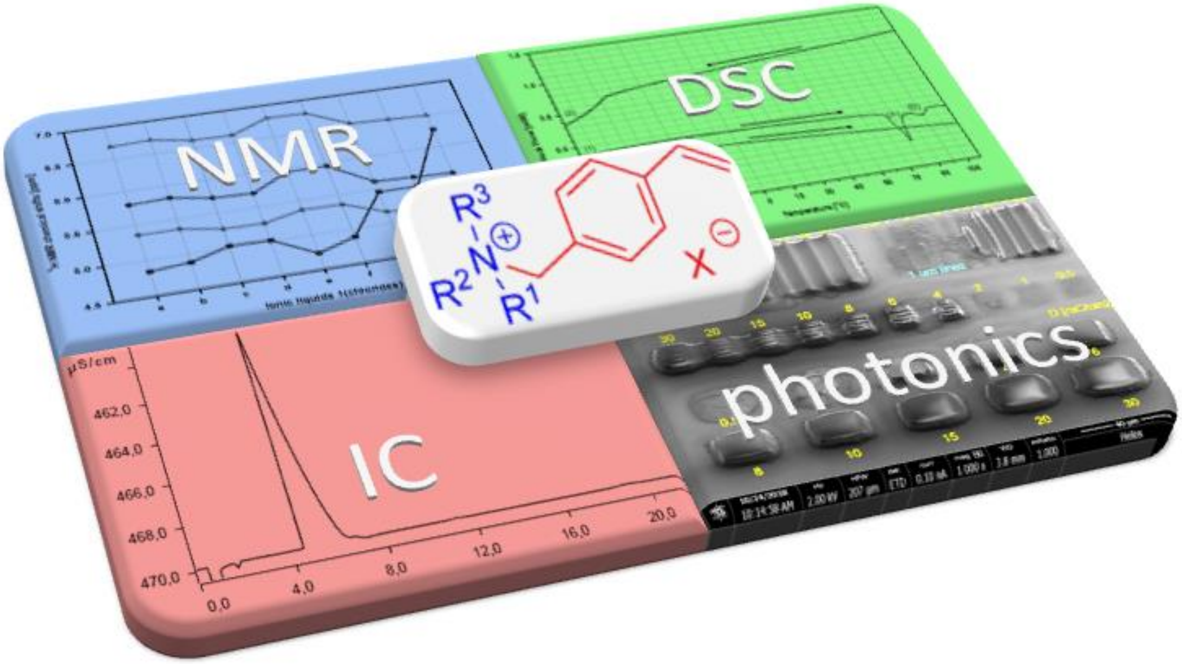
[1] *Materials Synthesis Group, Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubiez 46, 61-612 Poznan*

[2] *Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 B, 61-614 Poznan, Poland*

[3] *PORT sp. z o.o., ul. Stablowicka 147, 54-066 Wroclaw*

[4] *Department of Optics and Photonics, Faculty of Fundamental Problems of Technology, ul. Wyb. Wyspianskiego 27, 50-370 Wroclaw University of Science and Technology, Wroclaw, Poland*

Corresponding authors: adrian.zajac@ppnt.poznan.pl; marcin.smiglak@gmail.com



Abstract: The syntheses and full spectral (NMR, MS, IR), thermal (DSC) and ion chromatographic characterization of two series of amine-derived ionic liquids bearing 4-vinylbenzyl substituent and having chloride or bis(trifluoromethanesulfonyl)amide anion have been presented. The analysis of the dependence between ^{1}H NMR chemical shift value of selected protons and the structure of cation and anion has been undertaken. Not described before in the literature results of ion chromatographic analysis of obtained compounds have been discussed. The polymerization potential of selected isolated compounds has been briefly described on the base of DSC measurements and electron beam polymerization experiments. Mentioned experiments revealed that presented ionic liquids are prone to polymerization both in solution and pure form under temperature (DSC) or electron beam irradiation to form solid polymeric products, at micrometer scale in the latter case.

Keywords: ionic liquids, polymerizable ionic liquids, NMR, ion chromatography, DSC, electron beam polymerization, photonics

Introduction

The research on ionic liquids has been continuing for many decades,[1] nevertheless they still attract unabated interest of the scientific community. It is due to their very interesting properties such as *e.g.* combination of hydrophilic and hydrophobic features, liquid state below 100 °C together with ionic structure, extremely low volatility, high chemical inertness, thermal stability and wide range of a structural diversity. Their properties can be additionally adjusted by mixing with molecular liquids, such as water or organic solvents.[2] All of this characteristics predestine these compounds to play significant role in many fields,[3] *i.a.* as green solvents in small molecules reactions,[4] solvents for biopolymers,[5,6] polymerizations,[7,8] catalyses,[9,10] biocatalyses,[11] and enzymatic resolutions,[12] as convenient extraction solvents for organic compounds[13,14,15] and metals,[16,17,18] as liquid membranes,[19] mobile and stationary phase additives in liquid chromatography,[20,21,22] catalysts,[23,24] electrochemical sensors,[25,26,27,28] conducting factors in energy storage and conversion materials and devices (batteries, solar cells, supercapacitors),[29,30,31,32,33] energetic materials,[34,35,36,37] lubricants,[38] silk dyeing accelerating agents,[39] bacteri- and fungicidals,[40] plant systemic acquired resistance inducers,[41,42,] drug delivery tools,[43] solvents for polymorphic drugs transformations[44,45] and pharmaceuticals,[46,47] just to name few. Another significant advantage of ILs is a simplicity of their synthesis. Numerous known synthetic procedures are highly efficient and facile, resistant to ambient factors such as humidity or oxygen and characterized by high level of atom economy (often reaching 100%).[48,49] Substrates used are usually inexpensive and commercially available.

Potentially polymerizable ionic liquids bearing unsaturated substituent(s) seem to attract increasing attention in particular. They can combine all of the characteristics of an ionic liquid state and potentially available corresponding polymer. Many polymers of that kind are known and utilized, most of all, as conductive polymers[50,51,52,53,54,55] but also in large variety of applications, *e.g.*, surfactants,[56] sorbents,[57,58] electrocatalysts,[59] membranes,[60,61] GC stationary phases,[62] molecularly imprinted polymers,[63] light-emitting cells,[64] UV-imprint resists[65] and dental compositions.[66]

It is well-known from the literature that the common feature of polymerizable ionic liquids is the presence of terminal double bond in one or more substituents of ionic core, cationic in most cases.[67,68,69] The presence of terminal double bond is significantly convenient in those compounds due to the relative simplicity of its introduction to the ionic liquid structure and its predisposition to radical polymerization processes.

Polymerized ionic liquids or ionic polymers can be obtain in three main ways: (i) radical polymerization of ionic liquid monomers, (ii) post-polymerization processing of neutral polymers and (iii) copolymerization by cross-linking of existing polymeric ionic liquid chain with another one.[69] Two latter methods are not the subject of this article, therefore we focus on the radical polymerization. In general, the method is implemented by the addition of a proper initiator (e.g. AIBN) and the use of heating or UV irradiation of the reaction mixture.[69] Polymeric ionic liquids can also be successfully synthesized by: (i) reversible addition fragmentation transfer polymerization and (ii) radical polymerization mediated by atom transfer, cobalt, copper, nitroxide, methyl methacrylate, organometallics *etc.*[69]

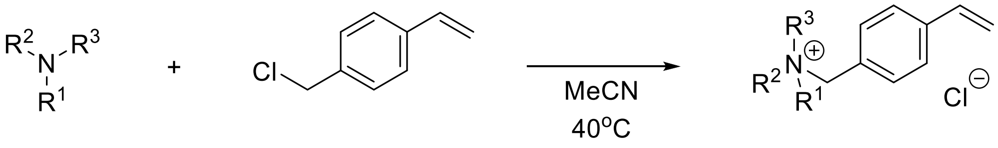
Herein we would like to present syntheses and full characterization of series of unsaturated amine-derived ionic liquids bearing 4-vinylbenzyl moiety. We chose this group of compounds due to the wide availability and low cost of substrates [selected amines, 4-vinylbenzylchloride, lithium bis(trifluoromethanesulfonyl) amide], and the presence of easily polymerizable styrene moiety in the ionic liquids structures, which should ensure its effective polymerization. The selection of amines was dictated by their availability, various chemical character (linear aliphatic, cyclic aliphatic and aromatic) and relatively high reactivity in quaternization reactions according to our experimental experience. Only few of them are known in literature, but, even then, their spectral data is considerably limited, usually to single NMR spectrum.[70] This paper is an attempt to create comprehensive, in established frames, set of synthetic procedures and characteristics of mentioned above and not yet fully described in literature compounds.[71,72,73] Initiator-less polymerization potential also is shortly presented on the basis of DSC analysis and results of preliminary experiments with electron beam polymerization processes.

Results and Discussion

Synthesis

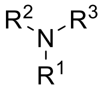
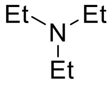
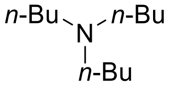
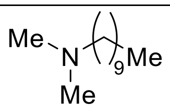
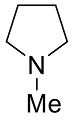
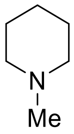
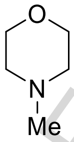
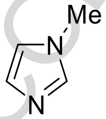
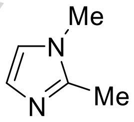
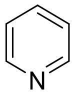
First, we had to synthesize a set of chloride forms **1a-i**. In order to achieve that we conducted quaternization reactions of selected aliphatic and aromatic amines **2a-i** with 1 eq. of 4-vinylbenzyl chloride **3** in MeCN, as a reaction medium, at elevated temperature. A reaction progress was determined by means of ion chromatography measurements of the reaction mixture. The temperature had to be kept below 40°C, because above that value spontaneous polymerization processes were observed. The product(s) of the process haven’t been further investigated due to its “side-effect” character and the fact that following publication is not focused on the topic of a batch polymerization. Moreover, due to this limitation reaction times were relatively long, particularly in the case of compounds **1c** and **1d**. Reactions furnished desired products **1a-i** in good to excellent yields, quantitatively in three cases (**Scheme 1**, **Table 1**). Products were obtained in pure form without further purification, and atom economy for all substrates was equal to 100%.

SCHEME 1. Synthesis of chlorides **1**.



2 **3** **1**

TABLE 1. Characterization of products **1a-i** of quaternization reaction showed in Scheme 1.

Compound		Reaction time [h]	Yield [%]	m.p. [°C]
1a		93	94 (lit. 75[71])	>350[a] (lit. 186-190[71])
1b		68	99 (lit. 69[71])	94.3 (lit. 133-135[71])
1c		239	99	47.2
1d		286	94 (lit. 90[72])	-42.4[b,c]
1e		139	98	86.4
1f		20	98	>350[a]
1g		167	99 (lit. 80[71])	84.4 -60.4[b]
1h		167	90	115.9 -44.0[b]
1i		91	97	163.5

[a] m.p. near to decomposition temperature, determined visually using capillary melting point apparatus (due to limited maximum measurement temperature of available DSC equipment)

[b] glass transition temperature

[c] lack of DSC peak attributed to m.p., most probably due to very high viscosity of the sample

Generally, 4-vinylbenzyl chloride is less reactive than allyl chloride[74] according to significantly longer reaction time: for 4-vinylbenzyl chloride reaction times were twice to six times longer than in a case of allyl chloride. The most reactive seemed to be amine **2f**, which reaction took only 20 hours till completion, and the least reactive were amines **2d**, **2g** and **2h**. Differences between melting points measured and given in the literature (see **Table 1**) could arise from the imperfection of the visual melting point indication method. A DSC method used during presented research is more precise due to independence on a human eye imperfection errors. For compounds **1a**, **1b**, **1d** and **1g** there was no further information in the literature concerning reaction times. Moreover, for compounds **1d** and **1g** melting point values are absent in the literature, either.

It also can be noticed that some of synthesized compounds (**1a**, **1f**, **1h**, **1i**) do not fulfill the definition of ionic liquids as an ionic compounds demonstrate melting point below 100°C. Nonetheless, these products are also presented as a part of the series, proving that the presence of relatively small chloride anion with localized negative charge increases a mutual coordination of both ions, thus favors a crystal lattice formation.

As a next step, we prepared a series of corresponding bis(trifluoromethanesulfonyl)amides **4a-i** in the simple and highly effective anion exchange reaction using aqueous solution of lithium bis(trifluoromethanesulfonyl)amide (LiNTf$_2$) and previously obtained chlorides **1a-i** as substrates (**Scheme 2**, **Table 2**). The presented process was almost instant in mild condition – transformation was completed in minutes in mixture of water and dichloromethane (DCM) at room temperature. Yield of these processes should be higher than 95%, nevertheless isolated yields were lower. It was caused by an abandonment of further washing of combined water layers with fresh portions of DCM, which activity would increase isolated yields (counted in relation to cation), however it would also increase the amount of inorganic impurities in the final product. Presented manner of work-up was optimal in terms of the yield/purity relation.

SCHEME 2. Synthesis of amides **4**.

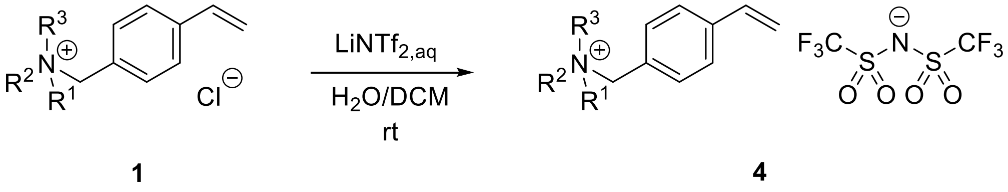
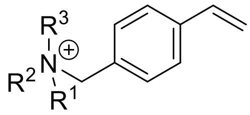
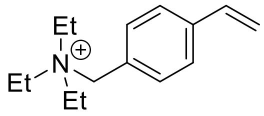
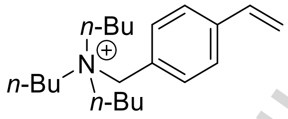
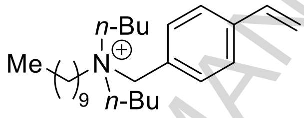
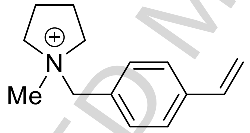
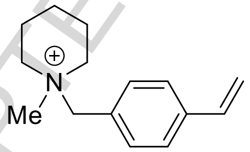
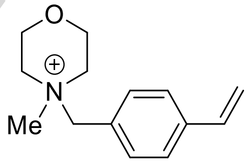
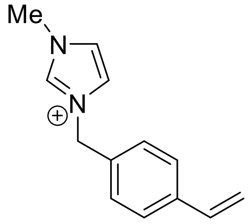
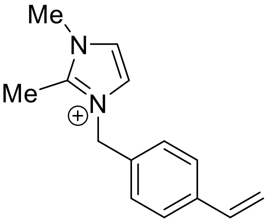
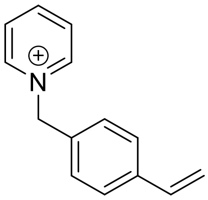


TABLE 2. Characterization of products **4a-i** of anion exchange reaction showed in Scheme 1.

Compound		Yield [%]	m.p. [°C]
4a		73 (lit. 70[70])	-42.8[a,b]
4b		79	-29.3[a] 64.3
4c		75	-63.2[a,b]
4d		72	-52.7[a,b]
4e		91	-40.6[a,b]
4f		93	76.3
4g		82	-53.6[a] 38.8

4h		85	-43.7[a,b]
4i		89	50.2

[a] glass transition temperature

[b] lack of DSC peak attributed to m.p., most probably due to very high viscosity of the sample

Considering chemical yields, chlorides **1a-i** were less reactive than analogous allyl substituted chlorides,[74] which can be explained in terms of higher steric hindrance generated by bulky 4-vinylbenzyl group. Relatively low yields were observed for more polar aliphatic ammonium cations (compounds **4a-c**) and pyrrolidinium cation (compound **4d**) – 73%, 79%, 75% and 72%, respectively, whereas for others isolated yield was higher. The tendency could be the result of higher solubility of compounds **4a-d** in water in comparison to **4e-i**, as a result of lower polarity and lower water affinity of cation for the latter group. In another words, the partition coefficient for the H_2O/DCM system of presented compounds **4a-i** was higher for more polar species **4a-d**. This behavior resulted in the loss of certain amount of product for a water phase, which was rejected. For the only one compound of this series described in the literature, namely **4d**, melting point was not given by the authors.[70]

Ion chromatography analysis

In order to achieve the final confirmation of the purity of obtained ionic liquids, ion chromatography (IC) analysis was performed. Due to its accuracy and versatility, the method, in most cases, ensures reliable and consistent results in terms of ionic liquids purity confirmation. Measurements were conducted for both cation and anion at set conditions (see Experimental section). Obtained results for cations are presented in **Table 3** and herein they are firstly reported in the literature. There is no IC data for anions presented in form of a table due to the fact that it is well known in the literature.[75,76]

TABLE 3. Data obtained for cations from ion chromatography analysis.

Compound no.	Retention time t_R [min]	Peak area a [(μS/cm)min]	Peak height h [μS/cm]	Purity[a] [%]
1a	13.59	0.812	0.637	>99.99
1b	21.01	0.717	0.447	98.98
1c	16.08	0.256	0.260	97.06
1d	15.68	0.424	0.419	99.05
1e	17.10	0.737	0.549	99.30
1f	10.34	3.975	2.838	>99.99
1g	9.22	18.536	9.138	99.85
1h	15.15	0.441	0,431	97.35
1i	12.44	5.081	2.555	>99.99
4a	13.80	6.400	3.415	98.30
4b	19.34	3.441	1.400	97.54
4c	16.29	0.064	0.046	96.91
4d	15.11	10.473	12.293	99.42
4e	16.92	3.725	1.782	>99.99
4f	10.60	3.165	2.384	>99.99
4g	9.73	5.004	3.198	>99.99
4h	14.78	3.209	1.855	>99.99
4i	12.09	5.448	3.119	99.26

[a] the highest value obtained from three repetitions of the synthetic procedure, all other obtained values were not lower by more than 0.2%

As it can be noticed, obtained results clearly indicated excellent purity of presented products at the level of ≥ 97%. In 7 cases the purity was higher than 99.99%. There was no unambiguous retention time changes tendency observed in relation to cation structure. The lowest retention time value was recorded for 1-methyl-3-(4′-vinylbenzyl)imidazolium cation (9.22 min.), and the highest – for tributyl-

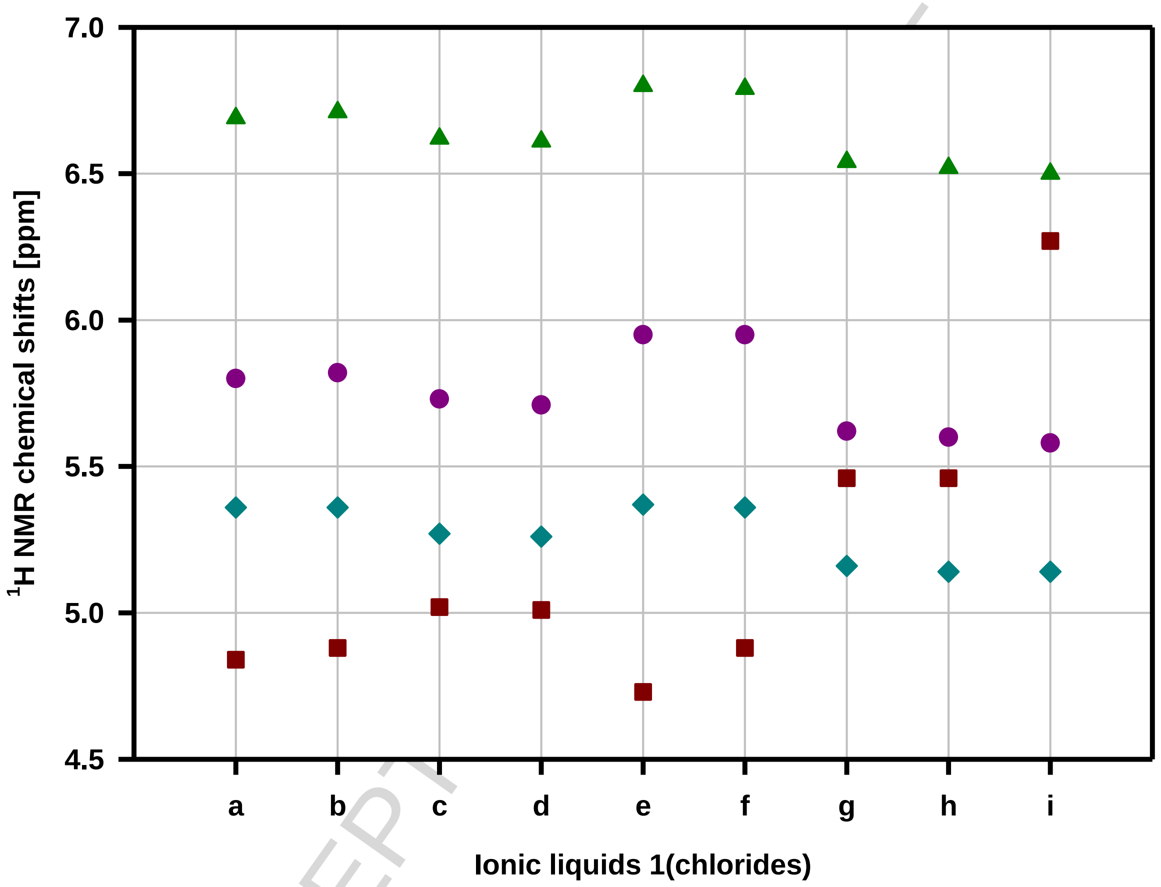
(4-vinylbenzyl)ammonium cation (21.01 min.) which fact makes the latter the most hydrophobic one in the series. To evaluate the quality of separation, capacity and asymmetry factors were calculated. For all analyzed samples the capacity factor value remained between 1 and 5, while the asymmetry factor – below 2.5.

IC analysis of anions gave similar results in terms of purity. Obtained retention time values were in the range of 5.10 – 6.78 min. for chloride anion and 17.89 – 19.13 min. for bis(trifluoromethanesulfonyl)amide anion. The results stayed in agreement with the literature,[75,76] and certain deviations were the result of slightly different separation conditions (eluent composition, column type).

NMR analysis

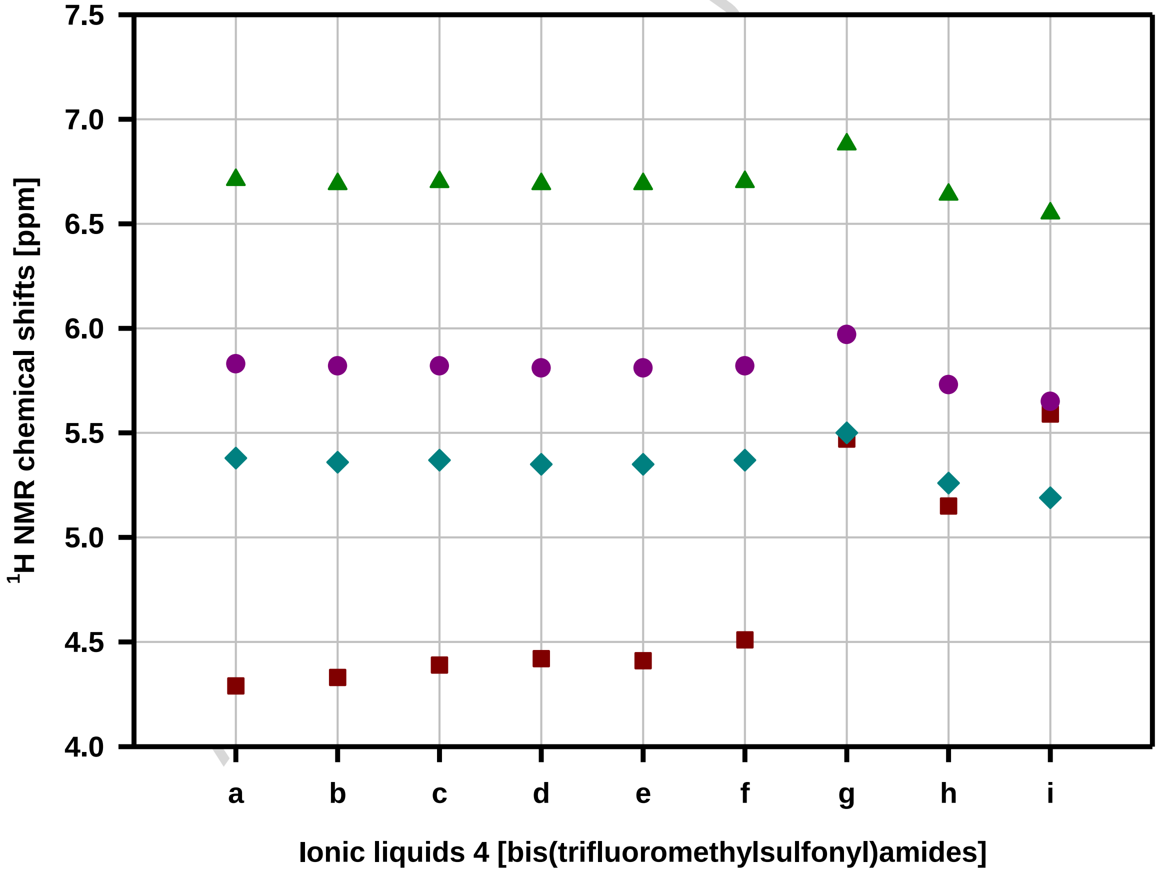
The analysis of ^{1}H NMR chemical shift value dependence of vinylbenzyl group aliphatic protons on the structure of chloride ionic liquids **1** cation (**Figure 1**) revealed conspicuous upward trend only for the chemical shift of benzyl methylene group protons in the series of triethylammonium **1a**, tributylammonium **1b**, decyldimethylammonium **1c**, pyrrolidine **1d**, piperidine **1e**, morpholine **1f**, 3-methylimidazole **1g**, 2,3-dimethylimidazole **1h**, pyridine **1i** cations, especially significant for aromatic compounds **1g-i** region of the curve. There was no trend observed for chemical shift value changes of vinyl group protons. The “vinyl protons chemical shift value –cation structure” relationship results for these compounds created almost horizontal line, except for compounds **1e** and **1f**, which were characterized by slightly higher ^{1}H NMR chemical shift than all other chlorides **1**. Results obtained for methylene group protons can be explained in terms of increasing electron withdrawing character of cation structure, especially aromatic ones, thus its deshielding property towards this group of protons. Vinyl group protons, in turn, were too distant form cation core, and the vinylbenzyl substituent system was too rigid, to be electronically influenced by it, which resulted in no significant changes of their chemical shift values as a function of cation structure. Subtly increased chemical shift values of vinyl protons for compounds **1e** and **1f** can be treated as a measurement error.

FIGURE 1. The juxtaposition of ^{1}H NMR chemical shift values of allyl group protons for compounds **1a-i**. Legend: -■- benzyl –CH$_2$-; -▲- vinyl –CH=; -●- vinyl =CH-H(B) trans; -◆- vinyl =CH-H(B') cis.



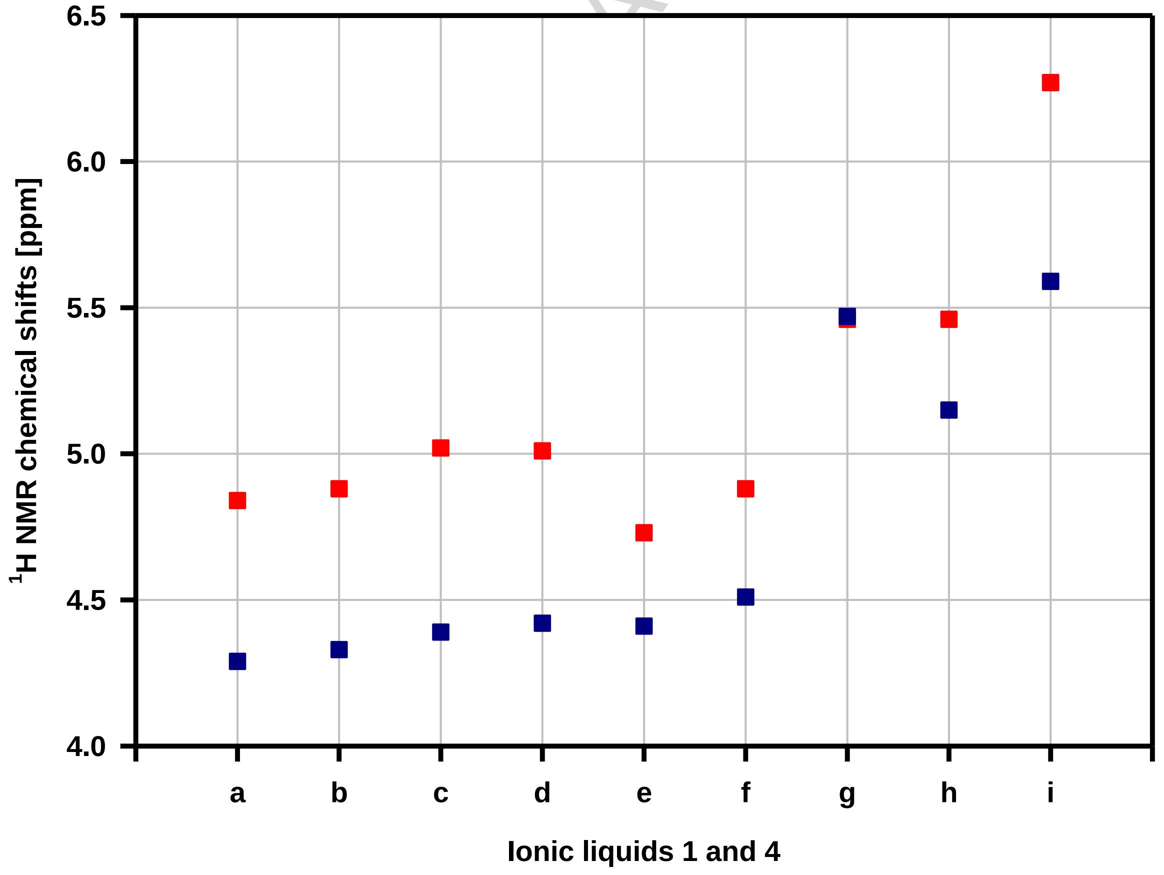
The analysis of ^{1}H NMR chemical shift value dependence of vinylbenzyl group protons on the structure of amide ionic liquids **4** cation (**Figure 2**) showed inconsiderable upward trend for the chemical shift of methylene group protons in the series of triethyl **4a**, tributyl **4b**, decyldimethyl **4c**, pyrrolidine **4d**, piperidine **4e** and morpholine **4f** cations, and then drastic increase of the value for 3-methylimidazole **4g**, 2,3-dimethylimidazole **4h**, pyridine **4i** ammonium cations. Chemical shifts value changes for other protons of vinylbenzyl group as a function of cation structure were almost imperceptible, creating nearly horizontal straight line. Very subtle increase of the value for compound **1g** can be treated as a measurement error. The increase of ^{1}H NMR chemical shift values of methylene group protons, as in the case of compounds **1**, was the result of the increase in electron withdrawing character of cation itself, which feature was the mostly observable for aromatic, thus strongly electron withdrawing cations of compounds **1g-i**. As it was described for chlorides **1**, the lack of the electronic influence of cation structure on vinyl protons chemical shift values was a result of too long distance between them and cation core and too rigid structure of vinylbenzyl substituent.

FIGURE 2. The juxtaposition of ^{1}H NMR chemical shift values of vinylbenzyl group aliphatic protons for compounds **4a-i**. Legend: -■- benzyl –CH_2-; -▲- vinyl –CH=; -●- vinyl =CH-H(B) trans; -◆- vinyl =CH-H(B’) cis.



In order to examine the influence of an anion present in an ionic liquid on the values of ^{1}H NMR chemical shift of vinylbenzyl group protons, the juxtaposition of these values for benzyl methylene group was prepared (**Figure 3**). The choice of this group was dictated by the most significant and visible changes of chemical shift values (see **Figure 1** and **Figure 2**). It is clear that trend line of chemical shift value changes for both chlorides **1a-i** and amides **4a-i** has very similar directional factor, thus similar rate of the increase of chemical shift value. Nevertheless, the comparison of chemical shift values for these protons between chloride ionic liquids **1** and amide ones **4** showed that values for chlorides **1** were on average 0.44 ppm higher than those recorded for amides **4**. The fact of such significant difference can be explained by stronger negative induction effect on these protons electronic density of chlorine atom than nitrogen atom.

FIGURE 3. The juxtaposition of ^{1}H NMR chemical shift values of methylene group protons for compounds **1a-i** and **4a-i**. Legend: -🟥- benzyl –CH_2- for compounds **1a-i**; -🟦- benzyl –CH_2- for compounds **4a-i**.



DSC analysis

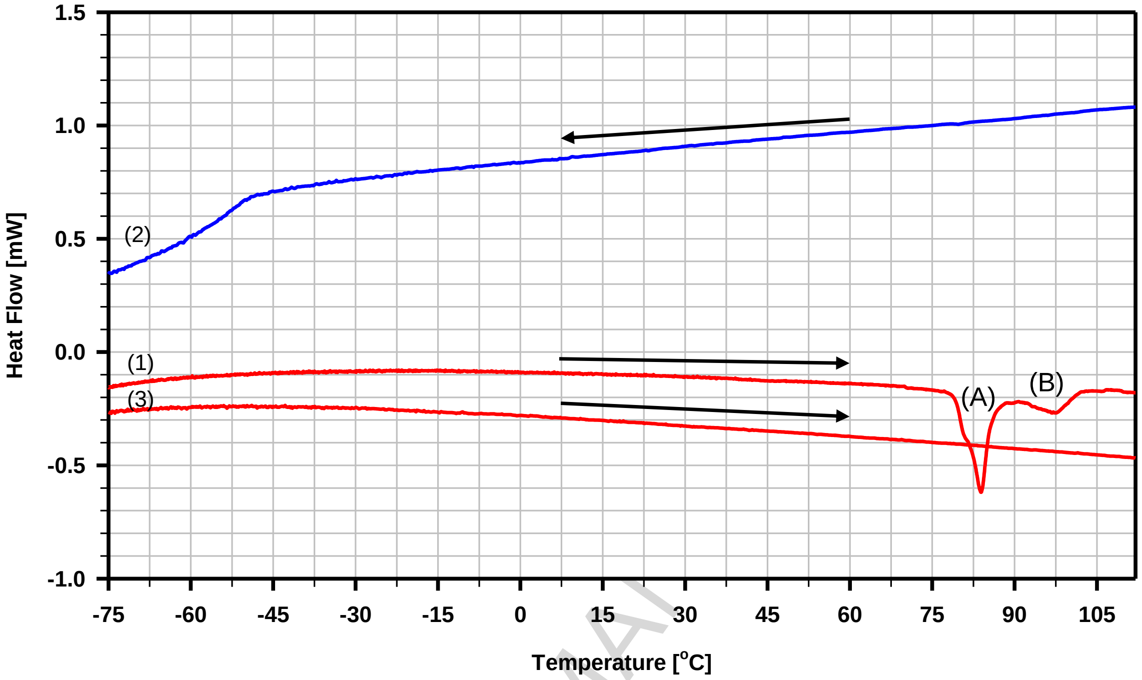
For all successfully obtained unsaturated amine-derived ionic liquids the differential scanning calorimetry analysis (DSC) have been performed to determine the thermal behavior of the sample (see **Table 1** and **2**). Only samples **1a**, **1f**, **1h** and **1i** have melting point above 100°C and thus cannot be classified as ionic liquids. Melting points of all other products (**1b**, **1c**, **1e** and **1g**) were in range of room temperature and 100°C. The exception was the sample **1d**, which was liquid at room temperature, but characterized only by glass transition temperature, which is more subtle physical change. The result was most probably due to very high viscosity of the sample.

The performed ion exchange significantly affects the melting temperature of the salts, mainly because of the difference in ion size and charge delocalization between chloride and bis(trifluoromethanesulfonyl)amide anions. The difference between the melting points of corresponding salts before and after ion exchange could be over 350°C. All of the obtained products have melting points below 77°C and could be classified as ionic liquids. Moreover, four out of nine samples (**4c-4e** and **4h**) are characterized by only glass transition temperatures and did not present any other thermal transitions on DSC thermograms in the investigated temperature range. The lack of DSC peak attributed to melting point was the most probably a result of very high viscosity of the sample.

Thermal polymerization process during DSC analysis

In the course of the characterization of obtained products we found that particularly the compound **1e** (1-methyl-1-(4′-vinylbenzyl)piperidinium chloride), due to its self-addition reaction ability, undergoes polymerization reaction. The polymerization could be observed as an endothermic signal on the DSC thermogram (B) just after the peak derived from the melting transition (A) (**Figure 4**). After this first cycle of heating to 120°C there are no signs of any thermal transition in the next cycle of cooling and heating, thus it is assumed that the test compound is subjected to a temperature-controlled polymerization process, which occurs at about 98°C.

FIGURE 4. DSC thermograms for **1e** compound. The number in brackets corresponds to a number of heating/cooling cycle. Legend: red lines – heating (range 2.5°C/min), blue line – cooling (range 2.5°C/min); (A) – melting transition peak, (B) – polymerization peak.

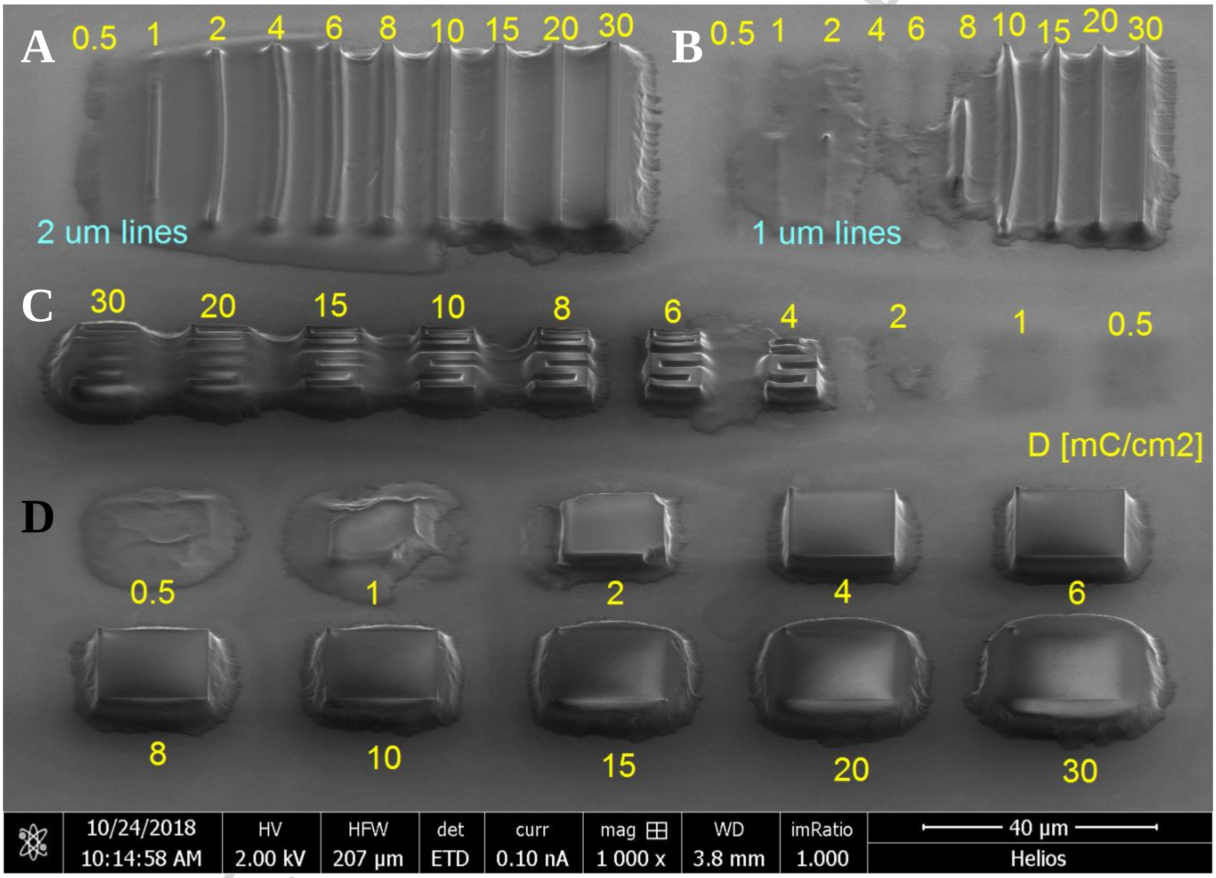


Electron beam irradiation induced polymerization

Having in mind this result we decided to examine the usefulness of described ionic liquids in the fabrication of polymeric photonic elements. That kind of structures play a significant role in many application areas including telecommunications, medicine, military and consumer equipment in forms of photonic integrated circuits, waveguides or microresonators. They are characterized by the low cost of manufacturing, broad bandwidth, tailorability and resistance to electrical noise.[77,78,79,80] The mentioned fabrication was performed using electron beam patterning technique, which included three general steps: (i) a preparation of an ionic liquid thin layer on silicon support by spinning, (ii) an irradiation of specified regions of the obtained thin layer by an electron beam, (iii) a development of fabricated polymerized photonic structures by washing with ethanol and drying with a stream of inert gas.

Compound **1g** was selected for this experiment due to excellent results obtained for its allyl analog.[81] The selection should allow to compare the behavior of these two analogs upon electron beam irradiation, thus determine the influence of the structure of polymerizable substituent on the polymerization efficiency and obtained polymeric structures topography. Four different irradiation patterns were performed at wide variety of electron dosage (**Figure 5**).

FIGURE 5. SEM images (52°-tilted view) of polymerized microstructures fabricated by irradiation of **1g** ionic liquid with various electron doses (0.5 – 30 mC cm^{-2}) at programmed patterns: A) lines of 2 µm thickness, B) lines of 1 µm thickness, C) open polygons and D) cuboids.

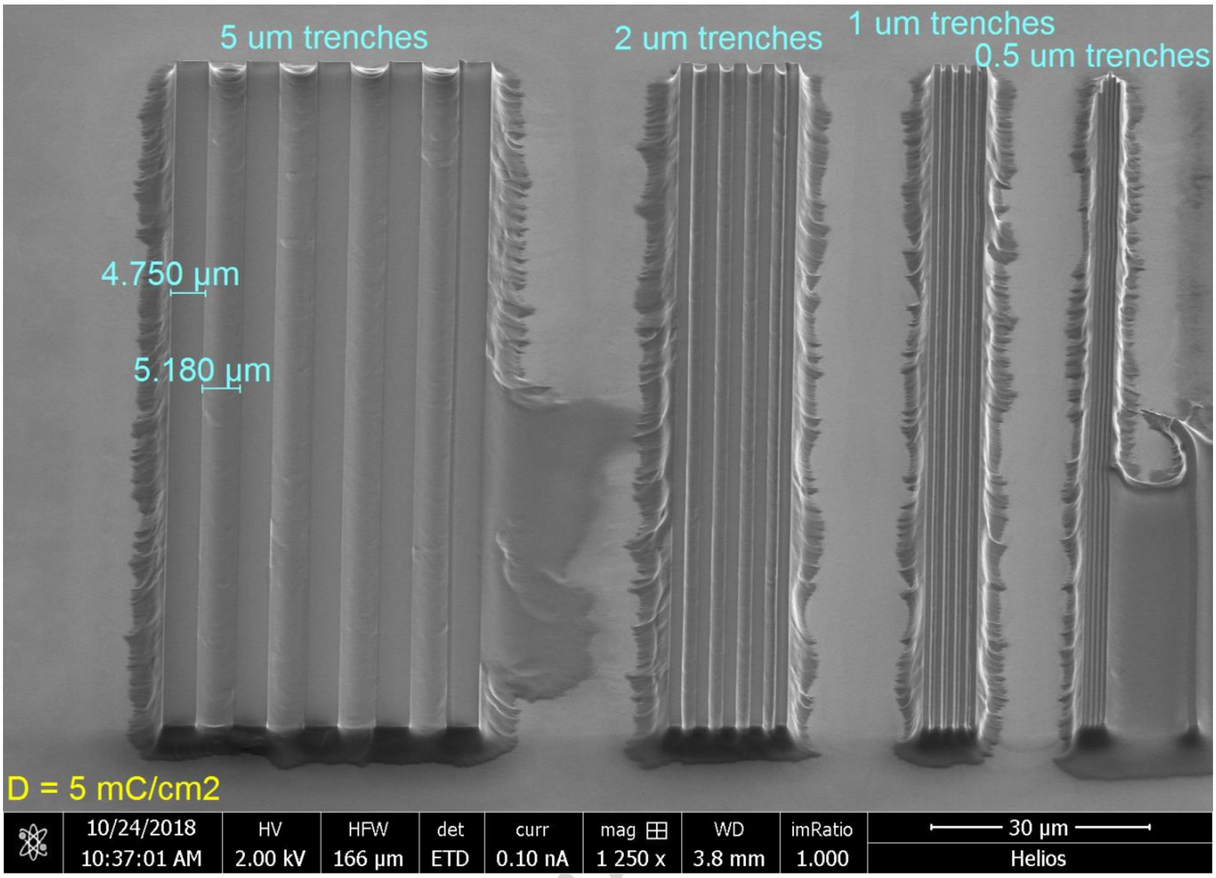


As it can be seen, even such small dose of electron beam irradiation as 0.5 mC cm^{-2} resulted in the polymerized formations, however the polymerization was not enough precise to obtain well-defined structures. We linked this process to heating of IL film by electron beam and subsequent flow of liquid reactants in the way that the polymerization of monomers occurred around the exposed area with only small contribution of the electron beam induced high resolution polymerization (visible as a desired structure shape). This thermal effect – strong for vinyl-based IL when compared with allyl-based IL[77] -

can be responsible for the improvement of the adhesion to the surface and, at the same time, the reduction of the resolution of the process. Relatively slow heating in the liquid resulted in the spread of hardening of the material. Second effect - high resolution polymerization caused directly by the beam is highly localized and needs perfect alignment of the irradiating beam. At low doses (up to about 2 mC cm^{-2}), the partial penetration of the beam into the thickness of the ionic liquid layer can result in the polymerization process occurrence only somewhere in the volume of the layer and the removal of the polymerized structure in the development process. It can be seen that for doses in range of 4-6 mC cm^{-2} both effects were balanced and the structure shape was well transferred to IL. When the electron dose was further increased, the structure shape became again more blurry due to the formation of undesired polymeric outgrowths outside of the exposure area. The similar effect of lateral widening of structures at high doses was also observed for allyl-based IL, for which the role of proximity effect caused by backscattered electrons should be also taken into account.[77]

On the base of above results the attempt of the fabrication of diffraction gratings of various line thickness at 5 mC cm^{-2} electron dose was undertaken (**Figure 6**).

FIGURE 6. SEM images (52°-tilted view) of polymerized diffraction gratings of various line thickness by irradiation of **1g** ionic liquid with 5 mC cm^{-2} electron dose.



It can be seen that edges of lines were regular, however lines separation was poor due to the formation of undesired polymeric outgrowths. The worth mentioning fact was that the line width was maintained and almost equal to programmed pattern, e.g. for programmed rectangles and trenches having width of 5 µm, obtained structure showed line width of 4.75 µm and trench width of 5.18 µm.

Taking into consideration the results obtained for allyl analog[81] of compound **1g**, it can be noticed that vinylbenzyl-substituted ionic liquid showed significantly higher tendency and readiness to polymerization than allyl-substituted one. For example, for allyl analog the minimal electron dose was equal to 10 mC cm^{-2}, and the optimal – 20-25 mC cm^{-2} [81] comparing to corresponding values for **1g**: 0.5 and 4-6 mC cm^{-2}, respectively.

Summarizing, on the basis of presented examples it can be stated that vinylbenzyl-substituent in cation structure caused significantly high polymerization potential of described ionic liquids. It was 5-10 times higher (referring to electron dose value) than for corresponding allyl analog. The problem of poor regularity of topography of electron beam polymerized elements is now under further investigation.

Conclusions

Herein we presented syntheses of 18 amine-derived ionic liquids having chloride or bis(trifluoromthanesulfonyl)amide anion and characterized their spectral (NMR, IR, MS), thermal (DSC) and ion chromatographic properties. We also shown the analysis of obtained ^{1}H NMR results for these compounds and demonstrated trends and nature of their dependence on the structure of both cation and anion of ionic liquids. We proved that the influence is negligible in cases of almost all of the protons of 4-vinylbenzyl group, except methylene group protons, which is directly bonded to cation core. The presence of chloride anion, featuring higher electronegativity and lower electron density delocalization in comparison with amide anion structure, caused significantly higher values of chemical shifts assigned to methylene group protons than for corresponding amides. The described compounds exhibit a high polymerization potential, which appeared in form of additional thermal polymerization peak during DSC analysis of compound **1e**. This characteristics was confirmed by the electron beam patterning experiment performed for compound **1g**. Moreover, the experiment revealed that vinylbenzyl-substituted ionic liquid **1g** is *ca.* 5-10 times easier polymerizable in terms of electron dosage than its allyl-substituted analog investigated previously.[81] The results are a good and valuable prognostic for the implementation of these compounds in polymeric photonic elements fabrication. This feature is under further investigation now.

Experimental section

All used reagents and solvents of high purity were commercially available and purchased.

NMR spectra were recorded using 400 and 500 MHz spectrometer in commercially available $CDCl_3$ solvent. IR measurements were conducted with utilization of diamond single crystal single reflection ATR system.

MS spectra and HRMS measurements were recorded using QTOF type mass spectrometer.

Melting point/glass transition analyses were determined by running DSC experiments with use of differential scanning calorimeter, cooled with an immersion cooler. The calorimeter was calibrated for temperature and cell constants using high purity indium (melting temperature: 156.7°C; specific enthalpy of melting: 28.71 J·g^{-1}) and zinc (melting temperature: 419.6°C; specific enthalpy of melting: -107.5 J g^{-1}). Data were collected at atmospheric pressure. The samples were initially cooled from room temperature, at a rate of 10 °C·min^{-1}, to -80°C. At this temperature, they were held for 10 min isotherm, prior to two cycles of heating and cooling at rates of 5 °C·min^{-1} spaced by 10 min isothermal holding at the lower (-80°C) and upper (50/120/150°C) endpoint temperatures. The upper endpoint temperature was set to 50°C for the samples that remain liquid at room temperature, 120°C for the samples that remain solid at room temperature and 150°C for the solid samples which did not present any thermal transition in the temperatures below 120°C. In a case of **1a** and **1f** the m.p. was determined using capillary melting point apparatus with visible detection at heating rate 10°C·min^{-1}. For all experiments, samples in the weight range between 10-15 mg were used in aluminium sample pans, sealed with lids with a pin hole. An empty sample pan served as the reference. The temperatures reported for the glass transition and melting were established as the onset and peak temperatures respectively, for the endothermic changes in heat flow.

Ion chromatography experiments were carried out using Metrohm Eco IC system (Metrohm, Herisau, Switzerland) equipped with 863 Compact IC Autosampler, 10.0 µl injection loop and conductometric detector (maintained at room temperature). Self-regenerating Suppressor Module (MSM) (Metrohm, Herisau, Switzerland), regenerated with distilled water and sulfuric acid, was used to separate and determine anions in ionic liquids. All data was recorded by Metrohm software. Cation ion chromatograph was equipped with Metrohm C4 ion exchange column (50 x 4.0 mm) coupled with a Metrosep C4 Guard. Anion ion chromatograph apparatus was equipped with a Metrosep A Supp 10 ion exchange column (150 x 4.0 mm) coupled with Metrosep A Supp Guard. A flow rate of 0.9 ml min^{-1} was used in both systems. Cation analysis was carried out using eluent composed of 30:70 ratio of acetonitrile (HPLC purity grade, Merck) and an aqueous solution containing 0.7 mM of dipicolinic acid and 1.7 mM of nitric acid (Merck). Anion separation was performed with eluent composed of

30:70 ratio of acetonitrile and an aqueous solution containing 3.2 mM of sodium bicarbonate and 1.0 mM of sodium carbonate (Merck). All aqueous solutions were prepared carefully using distilled water ($\sigma = 0.05$ µS cm^{-1}). During cation separation, average pressure in analytical system was maintained at the level of 3.5 MPa, whereas during anion analysis system worked under pressure of 13.5 MPa. Samples for anion analysis were prepared by uptake of filtered (0.2 µm filter) substance in quantity of 200 µl and then complemented in a vial with 10.0 ml of eluent. Samples for cation analysis was prepared by uptake 200 µl of filtered substance to a vial and then fulfilled with 2.0 ml of acetone (HPLC grade, Merck), 3.0 ml of nitric acid solution (concentration: 2.0 mM) and 5.0 ml of proper eluent. Before filtration, cation samples were dissolved in acetone and unreacted substrate (free amine) was protonated with nitric acid solution (concentration: 2.0 mM).

Water content was determined using Karl-Fischer type titration apparatus equipped with 800 Dosino dosing drive. For the measuring system dedicated chemicals, HYDRANAL® Titrant 2 and HYDRANAL® Solvent (Honeywell Fluka) were used. All analyses were carried out at room temperature with a drift value below value of 20.0 µl/min. Samples weight were determined with 0.1 mg accuracy. The average result from a minimum of three measurements was considered as the final result of the analysis.

Viscosity values [µ] were measured using rotary rheometer equipped with 40 mm Peltier steel plate, with shear rate of 200 s^{-1}, gap of 1000 µm and compression velocity of 100 µm·s^{-1} at 25°C.

Density values [d^{23}] of solids were indicated by hydrostatic balance method with use of toluene (for chlorides **1**) and water (for amides **4**) as a references at 23°C and ambient pressure. Density values [d^{23}] of liquids were measured using immersed standardized body method at 23°C and ambient pressure.

The commercially available monocrystalline silicon substrate, used as Si support in this research, was cleaned in the oxygen plasma (600 W) for 5 min. The thin film of the IL on Si support was formed by spin coating at 60 rps for 60 s. After the formation of the thin film, a substrate with the IL was placed in the SEM microscope, which was pumped to acquire a high vacuum, and then a sample was patterned by irradiation with an electron beam. The acceleration voltage of electrons was set to 30 kV. The electron dose was defined as:

$$D = \frac{I_B \times t_{dwell}}{x_{pitch} \times y_{pitch}}$$

where: I_B – electron beam current [nA], t_{dwell} – dwell time (exposure time of a one location point), x_{pitch} *and* y_{pitch} – distances between exposure points in a vertical and a horizontal directions (of screen), respectively (both values set at 50 nm). Samples were imaged using the SEM microscope.

Chlorides, General procedure A:

A solution of amine (1 eq) in MeCN was placed in two-neck round-bottomed flask equipped with a reflux condenser in one neck and septum in the other and heated to 40 °C with simultaneous stirring on magnetic stirrer. Then 4-vinylbenzyl chloride (1 eq) was added dropwise (with addition rate 5 mL/h). A resulting mixture was stirred at 40 °C for time required to complete the reaction. Next, the solvent was evaporated using rotary evaporator, and obtained product was washed with AcOEt (30 mL) in order to remove unreacted substrates and dried under vacuum to furnish pure ionic liquid.

Bis(trifluoromethanesulfonyl)amides, General procedure B:

Corresponding chloride (1 eq) was dissolved in distilled H_2O and transferred into separating funnel. Next, DCM was added, followed by aqueous solution of lithium bis(trifluoromethanesulfonyl)amide ($LiNTf_2$) (80%, 1.02 eq). Resulted mixture was shaked vigorously for a few minutes. Obtained layers were then separated, and organic layer was washed with distilled H_2O (twice) and H_2O with small addition of aqueous solution of $LiNTf_2$ (80%, 0.02 eq). The washing procedure was repeated as many times as it was needed to reach an absence of Cl^- ions in H_2O layer (checked by means of addition of aqueous solution of $AgNO_3$ to subsequent H_2O washes till no observable AgCl precipitation). After that the organic layer was evaporated under reduced pressure and dried under vacuum to give pure corresponding bis(trifluoromethanesulfonyl)amide ionic liquid.

Triethyl-(4-vinylbenzyl)ammonium chloride (1a)

Compound was obtained according general procedure A with use of triethylamine (2.83 g, 28.0 mmol), 4-vinylbenzyl chloride (3.82 g, 28.0 mmol) and MeCN (30 mL). Reaction time was equal to

93 h and the reaction gave pure product as a white solid (5.99 g, 94%), m.p. > 350°C, water content = 0.47 wt%, d^{23} = 1.120 g cm^{-3}.

IC: t_R = 13.59 min, purity > 99.99%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.43 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.69 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.80 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.36 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 4.84 (s, 2H, benzyl -CH_2-), 3.45 (q, $^3J_{HH}$ = 7.2 Hz, 6H, ethyl N-CH_2-), 1.46 (t, $^3J_{HH}$ = 7.2 Hz, 9H, ethyl Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.1 (vinyl -CH=), 135.6 (Ar), 132.9 (Ar), 127.2 (Ar), 126.5 (Ar), 116.5 (vinyl =CH_2), 61.5 (benzyl -CH_2-), 53.1 (ethyl N-CH_2-), 8.7 (ethyl Me).

IR (ATR, ν_{max}, cm^{-1}): 3074 (w), 2980 (vs), 1631 (w), 1607 (w), 1515 (m), 1478 (m), 1461 (s), 1411 (m), 1398 (s), 1295 (w), 1223 (w), 1186 (w), 1151 (m), 1099 (w), 1010 (vs), 945 (m), 904 (w), 863 (s), 808 (s), 787 (w), 688 (w), 586 (w).

MS (ESI): *m/z* (%) = 218 ($[M]^+$, 100), 117 ($[H_2C{=}CH\text{-}C_6H_4\text{-}CH_2]^+$, 7)

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{24}N^+$ 218.1909; Found 218.1909, Δ 0.

Tri-*n*-butyl-(4-vinylbenzyl)ammonium chloride (1b)

Compound was obtained according general procedure A with use of tri-*n*-butylamine (4.63 g, 25.0 mmol), 4-vinylbenzyl chloride (3.82 g, 25.0 mmol) and MeCN (40 mL). Reaction time was equal to 68 h and the reaction gave pure product as an yellow solid (8.38 g, 99%), m.p. = 94.3°C, water content = 0.31 wt%, d^{23} = 0.968 g cm^{-3}.

IC: t_R = 21.01 min, purity = 98.98%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (AA′BB′ d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 7.45 (AA′BB′ d, $^3J_{HH}$ = Hz, 2H, Ar-H), 6.71 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.82 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.36 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 4.88 (s, 2H, benzyl -CH_2-), 3.37 – 3.25 (m, 6H, butyl N-CH_2-), 1.84 – 1.75 (m, 6H, butyl N-CH_2-CH_2-), 1.41 (sextet, $^3J_{HH}$ = 7.4 Hz, 6H, butyl Me-CH_2-), 0.99 (t, $^3J_{HH}$ = 7.4 Hz, 9H, butyl Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.6 (vinyl -CH=), 135.3 (Ar), 132.6 (Ar), 126.6 (Ar), 126.5 (Ar), 116.0 (vinyl =CH_2), 62.5 (benzyl -CH_2-), 58.3 (butyl N-CH_2-), 24.2 (butyl N-CH_2-CH_2-), 19.5 (butyl Me-CH_2-), 13.4 (butyl Me).

MS (ESI): *m/z* (%) = 302 ($[M]^+$, 100).

HRMS (ESI) *m/z*: Calcd for $C_{21}H_{36}N^+$ 302.2848; Found 302.2849, Δ -0.3308.

Decyldimethyl-(4-vinylbenzyl)ammonium chloride (1c)

Compound was obtained according general procedure A with use of decyldimethylamine (6.03 g, 32.6 mmol), 4-vinylbenzyl chloride (4.19 g, 32.6 mmol) and MeCN (40 mL). Reaction time was equal to 239 h and the reaction gave pure product as an orange solid (9.21 g, 99%), m.p. = 47.2°C, water content = 0.34 wt%, d^{23} = 0.966 g cm^{-3}.

IC: t_R = 16.08 min, purity = 97.06%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.35 (AA′BB′ d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 6.62 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.73 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.27 (d, $^3J_{B'A,cis}$ = 11.0 Hz, 1H, vinyl =CH-$H_{B'}$), 5.02 (s, 2H, benzyl -CH_2-), 3.50 – 3.41 (m, 2H, decyl N-CH_2-), 3.23 (s, 6H, N-Me), 1.76 – 1.66 (m, 2H, decyl N-CH_2-CH_2-), 1.24 – 1.15 (m, 14H, decyl chain), 0.80 (t, $^3J_{HH}$= 7.0 Hz, 3H, decyl Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.7 (vinyl -CH=), 135.7 (Ar), 133.5 (Ar), 126.8 (Ar), 126.7 (Ar), 116.1 (vinyl =CH_2), 67.1 (benzyl -CH_2-), 63.6 (decyl N-CH_2-), 49.5 (N-Me), 31.8 (decyl chain), 29.4 (decyl chain), 29.3 (decyl chain), 29.2 (decyl chain), 26.3 (decyl chain), 22.9 (decyl chain), 22.6 (decyl chain), 14.1 (decyl Me).

IR (ATR, ν_{max}, cm^{-1}): 2955 (m), 2924 (vs), 2854 (s), 1486 (w), 1467 (w), 632 (s), 537 (s), 506 (m).

MS (ESI): *m/z* (%) = 302 ($[M]^+$, 100).

HRMS (ESI) *m/z*: Calcd for $C_{21}H_{36}N^+$ 302.2847; Found 302.2846, Δ 0.3308.

1-Methyl-1-(4′-vinylbenzyl)pyrrolidinium chloride (1d)

Compound was obtained according general procedure A with use of 1-methylpyrrolidine (2.12 g, 25.0 mmol), 4-vinylbenzyl chloride (4.19 g, 25.0 mmol) and MeCN (30 mL). Reaction time was equal to 286 h and the reaction gave pure product as a yellowish dense oil (7.23 g, 94%), m.p. n.a., T_g = -42.4°C, water content = 0.39 wt%, d^{23} = 0.981 g cm^{-3}.

IC: t_R = 15.68 min, purity = 99.05%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (AA′BB′ d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 7.33 (AA′BB′ d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 6.61 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.71 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.26 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 5.01 (s, 2H, benzyl -CH_2-), 3.93 (dt, $^2J_{HH}$ = 12.7 Hz, $^3J_{HH}$= 6.9 Hz, 2H, pyrrolidine N-CH_2-), 3.60 (dt, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 4.8 Hz, 2H, pyrrolidine N-CH_2-), 3.14 (s, 3H, N-Me), 2.27 – 2.18 (m, 2H, pyrrolidine -CH_2-), 2.17 – 2.05 (m, 2H, pyrrolidine -CH_2-).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.6 (vinyl -CH=), 135.7 (Ar), 133.0 (Ar), 127.7 (Ar), 126.8 (Ar), 116.0 (vinyl =CH_2), 63.8 (pyrrolidine N-CH_2-), 60.9 (benzyl -CH_2-), 45.6 (N-Me), 19.2 (pyrrolidine -CH_2-).

IR (ATR, ν_{max}, cm^{-1}): 3394 (bs), 2971 (vs), 2895 (m), 2249 (s), 1699 (s), 1630 (w), 1611 (m), 1514 (m), 1475 (vs), 1410 (s), 1374 (m), 1221 (m), 1039 (w), 1012 (w), 920 (s), 865 (m), 837 (m), 632 (bs), 533 (m).

MS (ESI): *m/z* (%) = 202 ($[M]^+$, 100) ,186 ($[M – CH_4 – H]^+$, 1), 139 (3), 117 ($[H_2C=CH-C_6H_4-CH_2]^+$, 6).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{20}N^+$ 202.1596; Found 202.1590, Δ 2.9680.

1-Methyl-1-(4′-vinylbenzyl)piperidinium chloride (1e)

Compound was obtained according general procedure A with use of 1-methylpiperidine (1.49 g, 15.0 mmol), 4-vinylbenzyl chloride (2.25 g, 15.0 mmol) and MeCN (30 mL). Reaction time was equal to 139 h and the reaction gave pure product as a white solid, partially precipitated during reaction course [2.36 g (precipitate) + 1.36 g (evaporated reaction mixture residue), 3.72 g, 98%], m.p. 86.4°C, water content = 0.45 wt%, d^{23} = 0.943 g cm^{-3}.

IC: t_R = 17.10 min, purity = 99.30%.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.60 (AA′BB′ d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 7.56 (AA′BB′ d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 6.80 (dd, $^3J_{AB,trans}$ = 17.7 Hz, $^3J_{AB′,cis}$ = 11.0 Hz, 1H, vinyl -CH=), 5.95 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H$_B$), 5.37 (d, $^3J_{B′A,cis}$ = 11.1 Hz, 1H, vinyl =CH-H$_{B′}$), 4.73 (s, 2H, benzyl -CH$_2$-), 3.45 – 3.32 (m, 4H, piperidinium -CH$_2$-N-CH$_2$-), 2.98 (s, 3H, Me), 1.93 – 1.77 (m, 4H, piperidinium -CH$_2$-), 1.92 – 1.58 (m, 1H, piperidinium -CH$_2$-), 1.53 – 1.44 (m, 1H, piperidinium -CH$_2$-).

^{13}C NMR (125 MHz, CDCl$_3$): δ = 138.7 (vinyl -CH=), 135.8 (Ar), 133.4 (Ar), 127.3 (Ar), 126.3 (Ar), 116.0 (vinyl =CH$_2$), 65.6 (benzyl -CH$_2$-), 59.4 (piperidinium -CH$_2$-N-CH$_2$-), 45.7 (N-Me), 20.7 (piperidinium -CH$_2$-), 19.3 (piperidinium -CH$_2$-).

IR (ATR, ν_{max}, cm^{-1}): 3079 (w), 3025 (m), 2968 (vs), 2902 (w), 2858 (w), 1628 (w), 1509 (w), 1483 (m), 1467 (m), 1440 (m), 1412 (m), 1389 (w), 1283 (w), 1223 (w), 1185 (w), 1120 (w), 1035 (w), 1016 (w), 990 (w), 974 (w), 943 (w), 925 (s), 907 (s), 861 (m), 835 (vs), 699 (w), 599 (w), 517 (w).

MS (ESI): *m/z* (%) = 216 ([M]$^+$, 100), 117 ([H$_2$C=CH-C$_6$H$_4$-CH$_2$]$^+$, 12).

HRMS (ESI) *m/z*: Calcd for C$_{15}$H$_{22}$N$^+$ 216.1752; Found 216.1757, Δ –2.3129.

1-Methyl-1-(4′-vinylbenzyl)morpholinium chloride (1f)

Compound was obtained according general procedure A with use of 1-methylmorpholine (2.53 g, 25.0 mmol), 4-vinylbenzyl chloride (3.82 g, 25.0 mmol) and MeCN (40 mL). Reaction time was equal to 20 h and the reaction gave pure product as a white solid, partially precipitated during reaction course [4.89 g (precipitate) + 0.91 g (evaporated reaction mixture residue), 6.22 g, 98%], m.p. > 350°C, water content = 0.40 wt%, d^{23} = 1.048 g cm^{-3}.

IC: t_R = 10.34 min, purity > 99.99%.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.60 (bs, 4H, Ar-H), 6.79 (dd, $^3J_{AB,trans}$ = 17.7 Hz, $^3J_{AB′,cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.95 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H$_B$), 5.36 (d, $^3J_{B′A,cis}$ = 11.4 Hz, 1H, vinyl =CH-H$_{B′}$), 4.88 (s, 2H, benzyl -CH$_2$-), 4.02 – 3.93 (m, 4H, morpholinium -CH$_2$-O-CH$_2$-), 3.63 – 3.55 (m, 2H, morpholinium N-CH$_2$-), 3.41 – 3.35 (m, 2H, morpholinium N-CH$_2$-), 3.14 (s, 3H, Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.8 (vinyl -CH=), 135.8 (Ar), 133.5 (Ar), 126.8 (Ar), 126.4 (Ar), 116.2 (vinyl =CH_2), 66.8 (benzyl -CH_2-), 59.8 (morpholinium -CH_2-O-CH_2-), 58.3 (morpholinium -CH_2-N-CH_2-), 44.8 (Me).

IR (ATR, ν_{max}, cm^{-1}): 3025 (s), 2971 (s), 2884 (m), 1626 (w), 1511 (m), 1491 (m), 1461 (m), 1407 (m), 1320 (w), 1249 (w), 1222 (w), 1202 (w), 1186 (w), 1159 (w), 1124 (s), 1116 (s), 1071 (m), 1043 (m), 1017 (w), 1007 (w), 968 (w), 958 (w), 934 (vs), 907 (vs), 882 (m), 862 (vs), 837 (vs), 704 (w), 566 (w), 520 (bw).

MS (ESI): *m/z* (%) = 218 ([M]$^+$, 100), 117 ([$H_2C=CH-C_6H_4-CH_2$]$^+$, 31).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{20}NO^+$ 218.1545; Found 218.1542, Δ 1.3752.

1-Methyl-3-(4′-vinylbenzyl)imidazolium chloride (1g)

Compound was obtained according general procedure A with use of 1-methylimidazole (7.00 g, 85.0 mmol), 4-vinylbenzyl chloride (12.97 g, 85.0 mmol) and MeCN (70 mL). Reaction time was equal to 167 h and the reaction gave pure product as an orange solid (19,81 g, 99%), m.p. = 84.4°C, water content = 0.39 wt%, d^{23} = 1.244 g cm^{-3}.

IC: t_R = 9.22 min, purity = 99.85%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.46 (s, 1H, imidazolium =N-CH=N-), 7.51 (t, $^3J_{HH}$ = 1.7 Hz, 1H, imidazolium –CH=), 7.40 (t, $^3J_{HH}$ = 1.7 Hz, 1H, imidazolium -CH=), 7.35 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.26 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.54 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB′,cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.62 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.46 (s, 2H, benzyl -CH_2-), 5.16 (d, $^3J_{B′A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B′}$), 3.93 (s, 3H, Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.6 (imidazolium =N-CH=N-), 135.6 (vinyl -CH=), 133.9 (Ar), 130.8 (Ar), 127.3 (Ar), 125.1 (Ar), 121.9 (imidazolium –CH=), 120.1 (imidazolium –CH=), 113.4 (vinyl =CH_2), 50.9 (benzyl -CH_2-), 34.6 (Me).

IR (ATR, ν_{max}, cm^{-1}): 3388 (bw), 3140 (w), 3061 (bw), 1631 (w), 1574 (w), 1516 (w), 1411 (w), 1165 (w), 832 (w), 635 (m), 576 (vs), 512 (s).

MS (ESI): *m/z* (%) = 199 ([M]$^+$, 100), 117 ([$H_2C=CH-C_6H_4-CH_2$]$^+$, 75).

HRMS (ESI) *m/z*: Calcd for $C_{13}H_{15}N_2^+$ 199.1235; Found 199.1233, Δ 1.0044.

1,2-Dimethyl-3-(4′-vinylbenzyl)imidazolium chloride (1h)

Compound was obtained according general procedure A with use of 1,2-dimethylimidazole (8.00 g, 83.0 mmol), 4-vinylbenzyl chloride (12.72 g, 83.0 mmol) and MeCN (70 mL). Reaction time was equal to 167 h and the reaction gave pure product as a white solid (18.54 g, 90%), m.p. = 115.9°C, water content = 0.38 wt%, d^{23} = 1.068 g cm^{-3}.

IC: t_R = 15.15 min, purity = 97.35%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (s, 2H, imidazolium -CH=CH-), 7.23 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.18 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.52 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.60 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.46 (s, 2H, benzyl -CH_2-), 5.14 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 3.82 (s, 3H, N-Me), 2.63 (s, 3H, Me).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1 (imidazolium =N-C=N-), 136.3 (vinyl -CH=), 133.8 (Ar), 130.6 (Ar), 126.6 (Ar), 125.0 (Ar), 121.0 (imidazolium –CH=), 120.0 (imidazolium –CH=), 113.3 (vinyl =CH_2), 50.0 (benzyl -CH_2-), 33.8 (N-Me), 8.8 (Me).

IR (ATR, ν_{max}, cm^{-1}): 3107 (w), 3057 (vs), 3007 (s), 2945 (m), 1633 (w), 1540 (m), 1539 (m), 1515 (m), 1411 (s), 1367 (m), 1342 (w), 1293 (m), 1252 (m), 1176 (m), 1124 (w), 1103 (w), 1038 (w), 1003 (m), 981 (w), 934 (m), 848 (w), 828 (m), 804 (w), 781 (m), 732 (w), 610 (w).

MS (ESI): *m/z* (%) = 213 ($[M]^+$, 100), 117 ($[H_2C=CH-C_6H_4-CH_2]^+$, 28).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{17}N_2^+$ 213.1392; Found 213.1396, Δ 1.8767.

1-(4′-Vinylbenzyl)pyridinium chloride (1i)

Compound was obtained according general procedure A with use of pyridine (3.96 g, 50.0 mmol), 4-vinylbenzyl chloride (7.63 g, 50.0 mmol) and MeCN (60 mL). Reaction time was equal to 91 h and the reaction gave pure product as an beige solid (11.27 g, 97%), m.p. 163.5°C, water content = 0.44 wt%, d^{23} = 1.013 g cm^{-3}.

IC: t_R = 12.44 min, purity > 99.99%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.80 (d, $^3J_{HH}$ = 6.0 Hz, 2H, pyridinium Ar-$H^{2,6}$), 8.32 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyridinium Ar-H^4), 7.92 (t, $^3J_{HH}$ = 6.8 Hz, 2H, pyridinium Ar-$H^{3,5}$), 7.64 (AA′BB′ d, $^3J_{HH}$ =

7.7 Hz, 2H, Ar-H), 7.22 (AA′BB′ d, $^{3}J_{HH}$ = 7.9 Hz, 2H, Ar-H), 6.50 (dd, $^{3}J_{AB,trans}$ = 17.5 Hz, $^{3}J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 6.27 (s, 2H, benzyl -CH_2-), 5.58 (d, $^{3}J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.14 (d, $^{3}J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.2 (Ar), 145.0 (Ar), 138.9 (vinyl -CH=), 135.6 (Ar), 132.7 (Ar), 129.8 (Ar), 128.3 (Ar), 127.1 (Ar), 115.6 (vinyl =CH_2), 63.5 (benzyl -CH_2-).

IR (ATR, ν_{max}, cm^{-1}): 3013 (vs), 2989 (m), 2964 (w), 2164 (w), 1637 (w), 1498 (w), 1470 (w), 1439 (w), 1234 (w), 1209 (w), 1120 (w), 1072 (w), 1041 (w), 1020 (w), 967 (w), 950 (w), 894 (w), 885 (w), 608 (w), 532 (w).

MS (ESI): *m/z* (%) = 196 ($[M]^+$, 100), 117 ($[H_2C{=}CH\text{-}C_6H_4\text{-}CH_2]^+$, 79).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}N^+$ 196.1126; Found 196.1127, Δ -0.5099.

Triethyl-(4-vinylbenzyl)ammonium bis(trifluoromethanesulfonyl)amide (4a)

Compound was obtained according general procedure B with use of triethyl-(4-vinylbenzyl)ammonium chloride (3.72 g, 14.67 mmol), distilled H_2O (20 mL), DCM (20 mL) and $LiNTf_{2,aq}$ (80%, 5.37 g, 14.97 mmol). For wash H_2O (2 × 10 mL) and H_2O (10 mL) with an addition of $LiNTf_{2,aq}$ (80%, 108 mg, 0.30 mmol) was used. The washing procedure was repeated twice. Pure product was obtained as a pale yellow very dense oil (5.32 g, 73%), m.p. = -42.8°C, water content = 0.04 wt%, d^{23} = 1.411 g cm^{-3}.

IC: t_R = 13.80 min, purity = 98.30%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (AA′BB′ d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.35 (AA′BB′ d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.71 (dd, $^{3}J_{AB,trans}$ = 17.6 Hz, $^{3}J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.83 (d, $^{3}J_{BA,trans}$ = 17.5 Hz, 1H, vinyl =CH-H_B), 5.38 (d, $^{3}J_{B'A,cis}$ = 11.0 Hz, 1H, vinyl =CH-$H_{B'}$), 4.29 (s, 2H, benzyl -CH_2-), 3.19 (q, $^{3}J_{HH}$ = 7.2 Hz, 6H, ethyl N-CH_2-), 1.40 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, ethyl Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.2 (vinyl -CH=), 135.4 (Ar), 132.4 (Ar), 127.2 (Ar), 125.4 (Ar), 119.9 (q, $^{1}J_{CF}$ = 321.2 Hz, CF_3), 116.6 (vinyl =CH_2), 60.5 (benzyl -CH_2-), 52.6 (ethyl N-CH_2-), 7.6 (ethyl Me).

IR (ATR, ν_{max}, cm^{-1}): 2995 (w), 1481 (w), 1398 (w), 1348 (m), 1178 (vs), 1134 (m), 1052 (m), 924 (w), 854 (w), 786 (w), 740 (w), 654 (w).

MS (ESI): *m/z* (%) = 218 ([M]$^+$, 100), 117 ([$H_2C{=}CH{-}C_6H_4{-}CH_2$]$^+$, 7)

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{24}N^+$ 218.1909; Found 218.1906, Δ 1.3749.

Tri-*n*-butyl-(4-vinylbenzyl)ammonium bis(trifluoromethanesulfonyl)amide (4b)

Compound was obtained according general procedure B with use of tri-*n*-butyl-(4-vinylbenzyl)ammonium chloride (8.80 g, 26.08 mmol), distilled H_2O (40 mL), DCM (40 mL) and $LiNTf_{2,aq}$ (80%, 9.54 g, 26.60 mmol). For wash H_2O (2 × 10 mL) and H_2O (10 mL) with an addition of $LiNTf_{2,aq}$ (80%, 187 mg, 0.52 mmol) was used. The washing procedure was repeated twice. Pure product was obtained as a pale yellow solid (12.01 g, 79%), m.p. = 64.3°C, water content = 0.03 wt%, d^{23} = 1.189 g cm^{-3}.

IC: t_R = 19.34 min, purity = 97.54%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.29 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.69 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.82 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.36 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 4.33 (s, 2H, benzyl -CH_2-), 3.08 – 3.00 (m, 6H, butyl N-CH_2-), 1.75 – 1.67 (m, 6H, butyl N-CH_2-CH_2-), 1.36 (sextet, $^3J_{HH}$ = 7.4 Hz, 6H, butyl Me-CH_2-), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 9H, butyl Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.2 (vinyl -CH=), 135.4 (Ar), 132.3 (Ar), 127.1 (Ar), 125.7 (Ar), 119.9 (q, $^1J_{CF}$ = 320.3 Hz, CF_3), 116.6 (vinyl =CH_2), 62.0 (benzyl -CH_2-), 58.1 (butyl N-CH_2-), 23.9 (butyl N-CH_2-CH_2-), 19.4 (butyl Me-CH_2-), 13.4 (butyl Me).

IR (ATR, ν_{max}, cm^{-1}): 3077 (w), 2970 (s), 1607 (w), 1517 (w), 1481 (w), 1464 (w), 1413 (w), 1400 (w), 1354 (s), 1223 (m), 1175 (vs), 1139 (m), 1047 (s), 946 (w), 865 (m), 832 (w), 809 (m), 789 (w), 741 (w), 690 (w), 613 (m), 568 (w), 541 (w).

MS (ESI): *m/z* (%) = 302 ([M]$^+$, 100).

HRMS (ESI) *m/z*: Calcd for $C_{21}H_{36}N^+$ 302.2848; Found 302.2849, Δ -0.6616.

Decyldimethyl-(4-vinylbenzyl)ammonium bis(trifluoromethanesulfonyl)amide (4c)

Compound was obtained according general procedure B with use of decyldimethyl-(4-vinylbenzyl)ammonium chloride (10.70 g, 31.70 mmol), distilled H_2O (40 mL), DCM (40 mL) and

$LiNTf_{2,aq}$ (80%, 11.60 g, 32.34 mmol). For wash H_2O (2 × 20 mL) and H_2O (20 mL) with an addition of $LiNTf_{2,aq}$ (80%, 230 mg, 0.64 mmol) was used. The washing procedure was repeated twice. Pure product was obtained as a pale yellow oil (13.89 g, 75%), m.p. n.a., T_g = -63.2°C, water content = 0.02 wt%, μ = 1.2785 Pa s, d^{23} = 1.313 g cm^{-3}.

IC: t_R = 16.29 min, purity = 96.91%.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.47 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.40 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.70 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.82 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.37 (d, $^3J_{B'A,cis}$ = 11.0 Hz, 1H, vinyl =CH-$H_{B'}$), 4.39 (s, 2H, benzyl -CH_2-), 3.27 – 3.19 (m, 2H, decyl N-CH_2-), 2.97 (s, 6H, N-Me), 1.81-1.72 (m, 2H, decyl N-CH_2-CH_2-), 1.35 – 1.20 (m, 14H, decyl chain), 0.87 (t, $^3J_{HH}$ = 6.9 Hz, 3H, decyl Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.3 (vinyl -CH=), 135.4 (Ar), 133.0 (Ar), 127.0 (Ar), 125.6 (Ar), 119.8 (q, $^1J_{CF}$ = 320.4 Hz, CF_3), 116.5 (vinyl =CH_2), 68.2 (benzyl -CH_2-), 64.5 (decyl N-CH_2-), 49.5 (N-Me), 31.8 (decyl chain), 29.3 (decyl chain), 29.2 (decyl chain), 29.1 (decyl chain), 28.9 (decyl chain), 26.0 (decyl chain), 22.7 (decyl chain), 22.6 (decyl chain), 14.0 (decyl Me).

IR (ATR, ν_{max}, cm^{-1}): 2956 (w), 2927 (w), 2857 (w), 1469 (w), 1349 (m), 1182 (vs), 1135 (m), 1054 (m), 860 (w), 740 (w), 654 (w), 616 (w), 570 (w), 513 (w).

MS (ESI): *m/z* (%) = 302 ($[M]^+$, 100), 186 ($[M – CH-C_6H_4-CH=CH_2]^+$, 1).

HRMS (ESI) *m/z*: Calcd for $C_{21}H_{36}N^+$ 302.2847; Found 302.2838, Δ 2.9773.

1-Methyl-1-(4′-vinylbenzyl)pyrrolidinium bis(trifluoromethanesulfonyl)amide (4d)

Compound was obtained according general procedure B with use of 1-methyl-1-(4′-vinylbenzyl)pyrrolidinium chloride (6.89 g, 35.68 mmol), distilled H_2O (30 mL), DCM (50 mL) and $LiNTf_{2,aq}$ (80%, 13.06 g, 36.40 mmol). For wash H_2O (2 × 10 mL) and H_2O (10 mL) with an addition of $LiNTf_{2,aq}$ (80%, 258 mg, 0.72 mmol) was used. Pure product was obtained as a yellow oil (10.00 g, 72%), m.p. n.a., T_g = -52.7°C, water content = 0.03 wt%, μ = 0.3449 Pa s, d^{23} = 1.257 g cm^{-3}.

IC: t_R = 15.11 min, purity = 99.42%.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.45 (AA′BB′ d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.41 (AA′BB′ d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 6.69 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.81 (d, $^3J_{BA,trans}$ =

17.6 Hz, 1H, vinyl =CH-H$_B$), 5.35 (d, $^3J_{B'A,cis}$ = 11.0 Hz, 1H, vinyl =CH-H$_{B'}$), 4.42 (s, 2H, benzyl -CH$_2$-), 3.65 – 3.58 (m, 2H, pyrrolidine N-CH$_2$-), 3.42 – 3.35 (m, 2H, pyrrolidine N-CH$_2$-), 2.91 (s, 3H, N-Me), 2.30 – 2.15 (m, 4H, pyrrolidine -CH$_2$-CH$_2$-).

^{13}C NMR (125 MHz, CDCl$_3$): δ = 140.2 (vinyl -CH=), 135.5 (Ar), 132.5 (Ar), 127.1 (Ar), 126.6 (Ar), 119.9 (q, $^1J_{CF}$ = 320.7 Hz, CF$_3$), 116.5 (vinyl =CH$_2$), 66.8 (pyrrolidine N-CH$_2$-), 63.3 (benzyl -CH$_2$-), 47.8 (N-Me), 21.1 (pyrrolidine -CH$_2$-).

MS (ESI): *m/z* (%) = 202 ([M]$^+$, 100), 117 ([H$_2$C=CH-C$_6$H$_4$-CH$_2$]$^+$, 14).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{20}N^+$ 202,1596; Found 202,1596, Δ 0.

1-Methyl-1-(4′-vinylbenzyl)piperidinium bis(trifluoromethanesulfonyl)amide (4e)

Compound was obtained according general procedure B with use of 1-(4′-vinylbenzyl)piperidinium chloride (5.00 g, 19.84 mmol), distilled H_2O (40 mL), DCM (40 mL) and LiNTf$_{2,aq}$ (80%, 7.26 g, 20.24 mmol). For wash H_2O (2 × 10 mL) and H_2O (10 mL) with an addition of LiNTf$_{2,aq}$ (80%, 143 mg, 0.40 mmol) was used. Pure product was obtained as a yellow oil (8.96 g, 91%), m.p. n.a., T$_g$ = -40.6°C, water content = 0.03 wt%, μ = 2.9662 Pa s, d^{23} = 1.384 g cm^{-3}.

IC: t_R = 16.92 min, purity > 99.99%.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.43 (AA′BB′, dd, $^3J_{HH}$ = 8.3 Hz, 4H, Ar-H), 6.69 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.81 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H$_B$), 5.35 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-H$_{B'}$), 4.41 (s, 2H, benzyl -CH$_2$-), 3.40 – 3.27 (m, 4H, piperidinium -CH$_2$-N-CH$_2$-), 2.91 (s, 3H, Me), 1.97 – 1.82 (m, 4H, piperidinium -CH$_2$-), 1.81 – 1.73 (m, 1H, piperidinium -CH$_2$-), 1.67 – 1.55 (m, 1H, piperidinium -CH$_2$-).

^{13}C NMR (125 MHz, CDCl$_3$): δ = 139.2 (vinyl -CH=), 134.5 (Ar), 132.2 (Ar), 126.0 (Ar), 124.2 (Ar), 118.9 (q, $^1J_{CF}$ = 321.8 Hz, CF$_3$), 115.5 (vinyl =CH$_2$), 67.8 (benzyl -CH$_2$-), 59.6 (piperidinium -CH$_2$-N-CH$_2$-), 44.9 (Me), 19.6 (piperidinium -CH$_2$-), 19.0 (piperidinium -CH$_2$-).

IR (ATR, ν_{max}, cm^{-1}): 1474 (w), 1347 (m), 1177 (vs), 1133 (m), 1051 (m), 994 (w), 932 (w), 857 (w), 789 (w), 740 (w), 654 (w), 613 (m), 569 (m), 514 (w).

MS (ESI): *m/z* (%) = 216 ([M]$^+$, 100), 117 ([H$_2$C=CH-C$_6$H$_4$-CH$_2$]$^+$, 10).

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{22}N^+$ 216,1752; Found 216,1754, Δ –0,9252.

1-Methyl-1-(4′-vinylbenzyl)morpholinium bis(trifluoromethanesulfonyl)amide (4f)

Compound was obtained according general procedure B with use of 1-(4′-vinylbenzyl)morpholinium chloride (3.82 g, 15.04 mmol), distilled H_2O (20 mL), DCM (20 mL) and $LiNTf_{2,aq}$ (80%, 5.50 g, 15.34 mmol). For wash H_2O (2 × 10 mL) and H_2O (10 mL) with an addition of $LiNTf_{2,aq}$ (80%, 108 mg, 0.30 mmol) was used. Pure product was obtained as a white solid (6.95 g, 93%), m.p. = 76.3°C, water content = 0.03 wt%, d^{23} = 1.423 g cm^{-3}.

IC: t_R = 10.60 min, purity > 99.99%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (AA′BB′, dd, $^3J_{HH}$ = 8.2 Hz, 4H, Ar-H), 6.70 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.82 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.37 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 4.51 (s, 2H, vinyl =CH-$H_{B'}$), 4.03 – 3.88 (m, 4H, morpholinium -CH_2-O-CH_2-), 3.55 – 3.46 (m, 2H, morpholinium N-CH_2-), 3.35 – 3.29 (m, 2H, morpholinium N-CH_2-), 3.11 (s, 3H, Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.9 (vinyl -CH=), 135.8 (Ar), 133.7 (Ar), 127.5 (Ar), 124.7 (Ar), 120.2 (q, $^1J_{CF}$ = 321.5 Hz, CF_3), 117.2 (vinyl =CH_2), 70.7 (benzyl -CH_2-), 60.8 (morpholinium -CH_2-O-CH_2-), 59.1 (morpholinium -CH_2-N-CH_2-), 46.1 (Me).

IR (ATR, ν_{max}, cm^{-1}): 1353 (m), 1336 (m), 1183 (vs), 1130 (m), 1054 (m), 993 (w), 961 (w), 926 (w), 900 (w), 867 (w), 834 (w), 739 (w), 606 (m), 569 (w), 513 (w).

MS (ESI): *m/z* (%) = 218 ($[M]^+$, 100), 117 ($[H_2C{=}CH{-}C_6H_4{-}CH_2]^+$, 32).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{20}NO^+$ 218,1545; Found 218,1547, Δ –0,9168.

1-Methyl-3-(4′-vinylbenzyl)imidazolium bis(trifluoromethanesulfonyl)amide (4g)

Compound was obtained according general procedure B with use of 1-methyl-3-(4′-vinylbenzyl)imidazolium chloride (10.89 g, 46.41 mmol), distilled H_2O (50 mL), DCM (50 mL) and $LiNTf_{2,aq}$ (80%, 16,98 g, 47.34 mmol). For wash H_2O (2 × 20 mL) and H_2O (20 mL) with an addition of $LiNTf_{2,aq}$ (80%, 334 mg, 0.93 mmol) was used. Pure product was obtained as a yellow solid (18.25 g, 82%), m.p. = 38.8°C, water content = 0.03 wt%, d^{23} = 1.480 g cm^{-3}.

IC: t_R = 9.73 min, purity > 99.99%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.95 (s, 1H, imidazolium =N-CH=N-), 7.63 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.52 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.47 (t, $^3J_{HH}$ = 1.9 Hz, 1H, imidazolium -CH=), 7.42 (t, $^3J_{HH}$ = 1.8 Hz, 1H, imidazolium -CH=), 6.88 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.97 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.50 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 5.47 (s, 2H, benzyl -CH_2-), 4.09 (s, 3H, Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.9 (imidazolium =N-CH=N-), 135.8 (vinyl -CH=), 135.7 (Ar), 131.5 (Ar), 129.1 (Ar), 127.2 (Ar), 123.8 (imidazolium –CH=), 122.1 (imidazolium –CH=), 119.7 (q, $^1J_{CF}$ = 321.0 Hz, CF_3), 115.5 (vinyl =CH_2), 53.1 (benzyl -CH_2-), 36.2 (Me).

IR (ATR, ν_{max}, cm^{-1}): 3153 (w), 3092 (w), 1562 (w), 1349 (m), 1177 (vs), 1161 (s), 1140 (m), 1051 (s), 1006 (w), 926 (w), 874 (w), 833 (w), 782 (w), 745 (w), 736 (w), 720 (w), 603 (m), 568 (m), 514 (w).

MS (ESI): *m/z* (%) = 199 ($[M]^+$, 100), 117 ($[H_2C=CH-C_6H_4-CH_2]^+$, 64).

HRMS (ESI) *m/z*: Calcd for $C_{13}H_{15}N_2^+$ 199.1235; Found 199.1230, Δ 2.5110.

1,2-Dimethyl-3-(4′-vinylbenzyl)imidazolium bis(trifluoromethanesulfonyl)amide (4h)

Compound was obtained according general procedure B with use of 1,2-dimethyl-3-(4′-vinylbenzyl)imidazolium chloride (8.93 g, 35.91 mmol), distilled H_2O (50 mL), DCM (50 mL) and $LiNTf_{2,aq}$ (80%, 13.14 g, 36.62 mmol). For wash H_2O (2 × 20 mL) and H_2O (20 mL) with an addition of $LiNTf_{2,aq}$ (80%, 255 mg, 0.71 mmol) was used. Pure product was obtained as an orange oil (15.06 g, 85%), m.p. n.a., T_g = -43.7°C, water content = 0.03 wt%, μ = 0.6106 Pa s, d^{23} = 1.342 g cm^{-3}.

IC: t_R = 14.78 min, purity > 99.99%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.17 (AA′BB′, d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.13 (d, $^3J_{HH}$ = 2.1 Hz, 1H, imidazolium -CH=), 7.03 (d, $^3J_{HH}$ = 2.1 Hz, 1H, imidazolium -CH=), 6.64 (dd, $^3J_{AB,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.73 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.26 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$), 5.15 (s, 2H, benzyl -CH_2-), 3.71 (s, 3H, N-Me), 2.52 (s, 3H, Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0 (imidazolium =N-C=N-), 138.4 (vinyl -CH=), 135.6 (Ar), 131.4 (Ar), 128.2 (Ar), 127.0 (Ar), 122.3 (imidazolium –CH=), 120.8 (imidazolium –CH=), 119.6 (q, $^1J_{CF}$ = 321.3 Hz, CF_3), 115.2 (vinyl =CH_2), 51.7 (benzyl -CH_2-), 35.0 (N-Me), 9.5 (Me).

IR (ATR, ν_{max}, cm^{-1}): 3149 (w), 1591 (w), 1515 (w), 1350 (s), 1331 (m), 1190 (vs), 1139 (m), 1056 (m), 656 (w), 633 (w), 619 (w), 571 (w), 544 (w), 535 (m).

MS (ESI): *m/z* (%) = 213 ($[M]^+$, 100), 117 ($[H_2C{=}CH\text{-}C_6H_4\text{-}CH_2]^+$, 21).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{17}N_2^+$ 213.1392; Found 213.1391, Δ 0.4692.

1-(4′-Vinylbenzyl)pyridinium bis(trifluoromethanesulfonyl)amide (4i)

Compound was obtained according general procedure B with use of 1-(4′-vinylbenzyl)pyridinium chloride (9.81 g, 42.34 mmol), distilled H_2O (40 mL), DCM (40 mL) and $LiNTf_{2,aq}$ (80%, 15.50 g, 43.19 mmol). For wash H_2O (2 × 10 mL) and H_2O (10 mL) with an addition of $LiNTf_{2,aq}$ (80%, 305 mg, 0.85 mmol) was used. Pure product was obtained as a yellow solid (17.96 g, 89%), m.p. = 50.2°C, water content = 0.04 wt%, d^{23} = 1.394 g cm^{-3}.

IC: t_R = 12.09 min, purity = 99.26%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (d, $^3J_{HH}$ = 5.8 Hz, 2H, pyridinium Ar-$H^{2,6}$), 8.31 (t, $^3J_{HH}$ = 7.8 Hz, 1H, pyridinium Ar-H^4), 7.86 (t, $^3J_{HH}$ = 7.1 Hz, 2H, Ar-$H^{3,5}$), 7.31 (bs, 4H, Ar-H), 6.55 (dd, $^3J_{BA,trans}$ = 17.6 Hz, $^3J_{AB',cis}$ = 10.9 Hz, 1H, vinyl -CH=), 5.65 (d, $^3J_{BA,trans}$ = 17.6 Hz, 1H, vinyl =CH-H_B), 5.59 (s, 2H, benzyl -CH_2-), 5.19 (d, $^3J_{B'A,cis}$ = 10.9 Hz, 1H, vinyl =CH-$H_{B'}$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.9 (Ar), 144.2 (Ar), 139.6 (vinyl -CH=), 135.6 (Ar), 131.0 (Ar), 129.7 (Ar), 128.7 (Ar), 127.5 (Ar), 119.8 (q, $^1J_{CF}$ = 321.9 Hz, CF_3), 116.1 (vinyl =CH_2), 64.9 (benzyl -CH_2-).

IR (ATR, ν_{max}, cm^{-1}): 3092 (w), 1637 (w), 1492 (w), 1350 (m), 1331 (m), 1226 (w), 1178 (vs), 1166 (s), 1141 (s), 1051 (s), 1008 (w), 939 (w), 872 (w), 756 (w), 724 (w), 681 (w), 601 (m), 568 (w).

MS (ESI): *m/z* (%) = 196 ($[M]^+$, 100), 117 ($[H_2C{=}CH\text{-}C_6H_4\text{-}CH_2]^+$, 58).

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}N^+$ 196,1126; Found 196,1125, Δ 0,5099.

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Highlights

1) the description of synthesis of 18 functionalized ionic liquids, mostly absent in literature;

2) the introduction of valuable for derivatization or polymerization unsaturated group;

3) the spectral, thermal and chromatographic characterization for obtained ionic liquids;

4) the chemical shift of selected groups and thermal properties strongly depends on the structure;

5) the obtained compounds have high polymerization potential at common and micrometer scale.