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Synthesis and properties of dicationic ionic liquids with pentasiloxane linker

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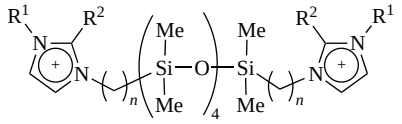
New dicationic ionic liquids with pentasiloxane linker between two imidazolium moieties and bis(trifluoromethylsulfonyl)imide anions were synthesized; their melting points, glass transition temperatures and viscosities were measured, and thermal and hydrolytic stabilities were investigated. The dependence of the properties of these ionic liquids on the length of the siloxane linker in the cation part is revealed.



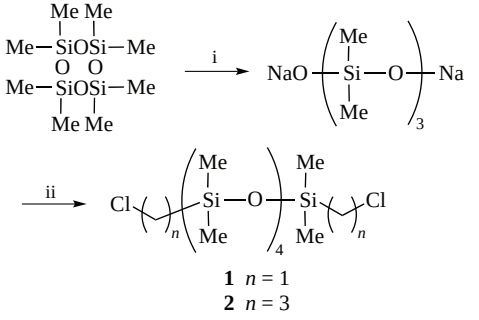
Keywords: dicationic ionic liquids, imidazolium compounds, pentasiloxane linker, thermal stability, viscosity, hydrolytic stability.

For the last quarter of a century, scientific and applied interest in ionic liquids (ILs), first of which was obtained in 1914,[1] has not subsided. Since 2013, about 6 000 articles and 2 000 patents devoted to this topic have been published annually.[2,3] Along with the traditional use of ILs in electrochemistry[4] and organic synthesis[5] as liquid media, there are also some exotic applications of ILs, such as plasticizers for solid propellants[6] and as lubricants for steel parts in spacecraft.[7,8] New ionic liquids are synthesized for storing carbon dioxide and nitrogen.[9,10] In recent years, software methods for predicting the IL properties depending on their 'architecture' have been intensively developed allowing the synthesis of ILs with a given set of properties.[11,12] Every year, the number of works devoted to the use of ILs in medicine as antibacterial agents,[13] solvents and drug delivery vehicles[14,15] increases. The current direction in development of environmentally friendly technologies is represented by works on the processing of plastics and cellulose employing ionic liquids.[16–18] A new direction has emerged in fine specific intermolecular interactions that lead to microstructures and dynamic inhomogeneities, which is important for IL application as specific solvents, electrolytes and functional materials.[19,20]

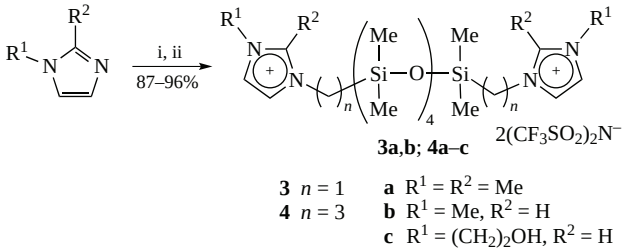
Dicationic ILs generally possess higher viscosity, higher thermal stability and lower volatility compared to monocationic ILs.[21–23] The presence of the second ion would cause an increase in the intermolecular interactions and, as a consequence, increase in the viscosity and melting point. Disiloxanes having highly mobile siloxane bond[24] were used as linkers to reduce the viscosity of dicationic ILs. Comparison of properties of dicationic ILs bearing disiloxane fragment in a linker with those having a polymethylene linker of similar length[25] did not reveal differences in their physico-chemical properties. Apparently, the nature of short-length linkers practically does not affect the properties of dicationic ILs.

This article is devoted to the synthesis and investigation of the properties of novel dicationic imidazolium bis(trifluoromethylsulfonyl)imide ILs with penta(dimethylsiloxane) linker. 1,2-Dimethylimidazole, 1-methylimidazole and 1-(2-hydroxyethyl)-imidazole were selected as the starting reagents as the resulting ILs differ in their ability to form hydrogen bonds influencing the intermolecular interactions between the ions of the ILs. Use of bis(trifluoromethylsulfonyl)imide (Tf_2N^-) anions can significantly reduce the viscosity of the target ILs. Due to the high mobility of siloxane bonds, two pentasiloxane linkers were selected which differed in the spacer length between imidazolium cation and the terminal silicon atom, namely, CH_2 and $(CH_2)_3$.

The synthesis of ILs was carried out in three stages (Schemes 1 and 2). At the first stage, a pentasiloxane linker was obtained, then the substituted imidazoles were quaternized with thus obtained α,ω-bis(chloroalkyl)siloxane, and after that the target bis(trifluoromethylsulfonyl)imide ILs were obtained from the chloride precursors by an ion exchange reaction. Penta(dimethylsiloxane) linkers **1** and **2** were prepared from disodium 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diolate (*cf.* refs. 26–30)



Scheme 1 *Reagents and conditions*: i, NaOH, MeOH, PhMe, boiling (ref. 31); ii, $Cl(CH_2)_nSi(Cl)Me_2$, PhMe, –20 °C.



Scheme 2 *Reagents and conditions*: i, linker **1** or **2**, MeCN, reflux; ii, $(CF_3SO_2)_2NLi$, MeCN, room temperature.

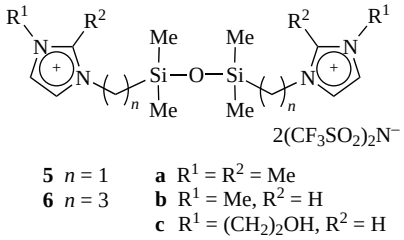


Figure 1 Structure of disiloxane dicationic ILs **5a–c** and **6a–c** (refs. 33, 34).

and the corresponding chloro(chloroalkyl)dimethylsilanes (see Scheme 1).

A feature of the synthesis of disodium 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diolate is its poor solubility in toluene.[31] It is obtained by treatment of octamethylcyclotetrasiloxane (D_4) with stoichiometric amounts of sodium hydroxide in refluxing methanol. After adding toluene and distilling off methanol and toluene–water azeotrope with a Dean–Stark trap, the target disodium diolate containing three silicon atoms is precipitated as a crystalline substance. This disodium salt is a product of rearrangement/cleavage of sodium α,ω-polydimethylsiloxanolates under the action of sodium hydroxide/sodium methoxide at the terminal silanolate groups. At the second stage of the linker synthesis, the terminal silanolate groups of the obtained trisiloxane were blocked with chloro(chloroalkyl) dimethylsilane, and dichlorides **1**, **2** were isolated by vacuum distillation.

The quaternization of substituted imidazoles with the obtained pentasiloxane linkers was carried out by refluxing in acetonitrile (see Scheme 2). Final anion exchange with lithium bis(trifluoromethylsulfonyl)imide was also performed in acetonitrile. The chloride precursors of ILs **3a**, **4a** and **3b** (stage i) are solids at room temperature. Chloride precursor of IL **4b** appears as a paste and does not flow while that of IL **4c** is a highly viscous fluid. All the listed chlorides are well soluble in water. When the reaction between 1-(2-hydroxyethyl)imidazole and pentasiloxane **1** with a chloromethyl group was attempted, the siloxane was destroyed and the corresponding product was not formed.

Table 1 presents the results of our studies of the properties of the dicationic ILs with a pentasiloxane linker by thermophysical methods. According to TGA data, the thermal stability practically does not change with an increase in the length of the siloxane linker from Si_2[33,34] (Figure 1) to Si_5. Ionic liquid **3a** based on 1,2-dimethylimidazole is characterized by the highest thermal stability (T_{destr} = 445 °C), as in the case of disiloxane IL **5a**. Elongation of the organic spacer between imidazolium cation and silicon atom from CH_2 to $(CH_2)_3$ (ILs **3a**,**b** *vs.* **4a**,**b**) and replacing the methyl group with a hydrogen atom at position 2 of the imidazolium cation (ILs **3a**, **4a** *vs.* **3b**, **4b**) lead to a decrease in the thermal stability by ~25–30 and ~20–25 °C, respectively (see Table 1). The change in thermal stability in the first case is explained by an increase in the proportion of methylene organics in the IL, and in the second case by the formation of a hydrogen bond between the relatively mobile hydrogen atom at the position 2 of the imidazolium cation and the Tf_2N^- anion, which promotes thermal decomposition.

A similar dependence of thermal stability on the length of the spacer and the presence of hydrogen atom at the position 2 of the imidazolium cation is also characteristic of disiloxane-based dicationic ILs (see Table 1). The introduction of hydroxy groups capable of forming additional hydrogen bonds does not lead to a decrease in the thermal stability of pentasiloxane ILs **4b** and **4c**, as in the case of disiloxane ILs **6b** and **6c**. The obtained data are explained by a decrease in the polarity of the siloxane bond in the pentasiloxane linker compared to the disiloxane one (Figure 2).

Analyzing DSC data for pentasiloxane ILs and comparing them with similar data for disiloxane-based ones, we can conclude that the elongation of the linker affords ILs which are less prone to crystallization and to a decrease in the glass transition temperature (see Table 1). In contrast to disiloxane ILs **5a**, **6a** prepared from 1,2-dimethylimidazole, having a T_m of 69 °C (methylene spacer) and 59 °C (propylene spacer), of pentasiloxane ILs only 1,2-dimethylimidazole-based IL **3a** with a methylene spacer is crystalline at room temperature. The T_m value of IL **3a** is 21 °C lower than that of the similar disiloxane IL **5a**. The T_g value of pentasiloxane ILs decrease by ~10–15 °C depending on the nature of the substituent compared to disiloxane ILs, and their values are from –61 to –68 °C. An increase in the siloxane linker length shifts the glass transition temperature of dicationic ILs towards the of polydimethylsiloxane T_g value.[32]

The pentasiloxane-linked ILs possess a significantly lower viscosity (see Table 1). This decrease is due to the nature of siloxane bonds, which are characterized by high mobility over a wide temperature range.[35] The viscosities of dicationic ILs with pentasiloxane linker are 1.5–1.8 times lower than those of ILs with disiloxane linker, and for the ILs based on 1-methylimidazole they are ⩽200 cSt at 30 °C.

The hydrolytic stability of siloxane linkers can be indirectly evaluated from the structure of the product of quaternization of 1-(2-hydroxyethyl)imidazole with α,ω-bis(chloromethyl)siloxanes. An ionic liquid with hydroxyethyl group was isolated

Table 1 Properties of pentasiloxane (Si_5) *vs.* disiloxane (Si_2) dicationic ionic liquids **3**–**6**.

ILs	Cation structure			$T_{destr.}$/°C (TGA)		T_g/°C (DSC)		Viscosity (30 °C)/cSt	
	R^1	R^2	*n*	Si_5	Si_2	Si_5	Si_2	Si_5	Si_2
3a/**5a**	Me	Me	1	445	437	48[a]	69[a]	–	–
4a/**6a**	Me	Me	3	417	419	–61	59[a]	485	–
3b/**5b**	Me	H	1	422	435	–66	–52	172	312
4b/**6b**	Me	H	3	398	402	–68	–58	201	344
–/**5c**[b]	$(CH_2)_2OH$	H	1	decomposed					
4c/**6c**	$(CH_2)_2OH$	H	3	407	391	–62	–53	399	602

[a] Melting point. [b] The lower homologue of **5c** (‘**3c**’) could not be obtained.

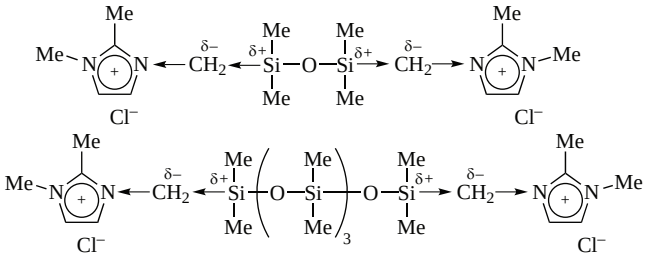


Figure 2 Polarity of bonds in the cations of disiloxane and pentasiloxane dicationic ILs (chlorides).

only when using pentasiloxane linker with propylene spacer, namely, **4c**. Upon the attempted synthesis of IL **3c** based on a pentasiloxane linker with methylene spacer, it was destroyed by the action of OH groups of 1-(2-hydroxyethyl)imidazole at the stage of quaternization. ^{29}Si NMR spectra of chloride precursors of IL **3c** and **4c** (see Online Supplementary Materials, Figure S1) confirm the conclusion. A significant number of peaks in the spectrum of this reaction mixture instead of three peaks corresponding to pentasiloxane (IL **4c**), indicates the occurrence of protolysis involving the OH groups of the reagent. However, impurity peaks in the ^{29}Si NMR spectrum of chloride precursor of IL **3c** are lower than in the spectrum of the products of reaction between 1-(2-hydroxyethyl)imidazole and disiloxane linker with chloromethyl groups (ILs **3c** and **5c**, Figures S1, S2). The higher protolytic stability of the pentasiloxane IL is explained by the lower polarization of siloxane bonds by imidazolium cations in the pentasiloxane linker compared to disiloxane one (Figure 2). This fact is observed only for linkers with methylene spacers. The induction effect of imidazolium cations which causes a strong polarization of the siloxane bond in the disiloxane linker almost completely disappears with an increase in the length of the spacer from methylene to propylene.

In summary, new pentasiloxane-based dicationic ionic liquids were synthesized. These ionic liquids are characterized by low glass transition temperature (~–70 °C), low viscosity (<200 cSt) and high thermal stability (>400 °C). Pentasiloxane dicationic ILs have greater hydrolytic stability than analogous disiloxane ILs due lower influence of imidazolium cations on the polarity of siloxane bonds.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.039.

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