

RESEARCH ARTICLE

Tuning the glass transition of siloxane-based poly(ionic liquid)s towards high ion conductivity

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Abstract

Herein, we report a simple and versatile synthetic approach towards siloxane-based poly(ionic liquid)s (PILs) with unusually low glass transition temperatures (T_g) down to -73°C , and thus “liquid-like” behavior at room temperature. We designed a polydimethylsiloxane-derived copolymer carrying dialkylimidazolium moieties, and by careful selection of the side-chain length and the type of anions we were able to manipulate its T_g over a wide range and reach high ionic conductivities (σ_{DC}) up to 4.8×10^{-5} S/cm at 300 K. The ionized species make up only a minor fraction (<25 mol%) of the overall repeating units and are supposedly randomly distributed: Yet our results indicate dramatic effects on the thermal properties due to repulsive interactions between ionic and non-ionic segments.

KEYWORDS

conductivity, glass transition temperature, poly(ionic liquid), polysiloxane

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1 | INTRODUCTION

Poly(ionic liquid)s (PILs) are permanently charged polymers, which carry ionic liquid (IL)-like species in their repeating units. Their excellent ion conduction properties and safe handling in particular make them promising candidates for quasi-solid state electrolytes in energy devices such as capacitors and transistors.¹

PILs are commonly considered as single-ion conductors, as either the anion or the cation species is covalently restricted to the polymer backbone, while the other one, the counter ion, is responsible for charge transport.¹ Hence, conductivity is mainly determined by the mobile counter ions.^{2–5} This is in contrast to their ionic liquid (IL) monomeric analogues, where both ions are able to move. Consequently, conductivity of PILs is generally at least two orders of magnitude lower than those of ILs, which currently limits their application as polymer electrolytes.^{2,6} However, the enormous variety of cation-anion pairs, and the vast possibilities of macromolecular design give rise to PILs with tunable properties in an unusually wide window.^{1,7–10} In fact, judicious choice of the ions and polymer backbone allows for designing “liquid-like” PILs, as recently demonstrated by us and other groups,^{11–15} which are of significant potential in polymeric ion conductors. For instant, Jourdain and coworkers elegantly combined a siloxane-based backbone with IL-like species as side-groups and the prepared ionic polymers with a T_g of -62°C and strongly enhanced conductivities up to $\sim 6.7 \times 10^{-5}$ S/cm at 30°C .¹¹ Such unique properties are due to the relatively small energy barrier for rotational motion around silicon-oxygen bonds, which promotes segmental movement of the siloxane units at low temperatures.¹⁶ It is therefore possible to create at room temperature “liquid-like” solvent-free ionic polymer materials by combination of pliable polysiloxanes with IL-like species. The scope of this methodology is also demonstrated by Liang and coworkers, who reported a siloxane-based PIL including phosphonium-type species that exhibited a T_g even below -70°C .¹⁷

To date, several groups have addressed this promising class of siloxane-based PILs and prepared polycations with ammonium,¹⁸ imidazolium,¹⁹ phosphonium¹⁷ and triazolium.¹¹ Some works have also focused on polysiloxane copolymers with both ionic and non-ionic segments (e.g., dimethylsiloxane units).^{17,19–22} A low concentration of ionic repeating units reduces the charge density but is generally favorable to achieve a low T_g , as polydimethylsiloxanes (PDMSs) exhibit the lowest T_g s among hitherto known polymer classes.¹⁹ It is worth noting that for such copolymers also repulsive interactions between the ionic and non-ionic segments could dramatically influence the thermal behavior and conduction properties.

In this article we present a fast and efficient route towards siloxane-based PILs with “liquid-like” behavior at room temperature due to their flexible backbone and a balanced amount of ionized repeating units. We further explore the impact of the type of counter anion and side-chain length on the thermal properties and succeed in tuning its T_g over a rather wide range far beyond conventional polyelectrolytes.

2 | RESULTS AND DISCUSSION

2.1 | Synthetic route

The most convenient strategy towards covalently linking imidazolium-based IL-like moieties to a polysiloxane backbone is via post-polymerization modification of commercially available polysiloxane derivatives. We chose the supposedly random copolymer poly[dimethylsiloxane-*co*-(chloropropylmethyl)siloxane] P(DMS-*co*-CMS) as precursor, which contains 14.8 mol% of the CMS unit, as determined by proton nuclear magnetic resonance spectroscopy (¹H-NMR). The chloropropyl groups of P(DMS-*co*-CMS) were modified by reaction with *n*-alkylimidazoles, as schematically shown in Figure 1. Specifically, 1-methylimidazole and 1-butylimidazole were used as the reagents. The former was utilized for an initial study to underline the feasibility of this approach, and its quaternization product is hereafter termed as C₁-PIM-Cl.

In a typical experiment, both precursors P(DMS-*co*-CMS) and 1-methylimidazole (20 mol eq. per Cl) were dissolved in *n*-butanol and the reaction mixture was heated up stepwise to its boiling point and kept under these conditions overnight (see Exp. section for details). To isolate the ionic product the reaction mixture was precipitated into diethyl ether, followed by at least two dissolution-precipitation steps in dichloromethane and diethyl ether, respectively. Finally, the oily product was dried at 80°C under high vacuum (10^{-3} mbar) to yield an almost colorless, viscous copolymer. The viscous nature of C₁-PIM-Cl is demonstrated in Figure S1, which shows photographs of the ionic copolymer in an upside-down glass container.

The chemical structure of C₁-PIM-Cl was determined by ¹H- and ¹³C-NMR spectroscopy. Figure 2(A) depicts the ¹H-NMR spectra of the ionic product (top) and its two precursors, the 1-methylimidazole and the neutral P(DMS-*co*-CMS) copolymer. The imidazolium proton signals (*Im-2* and *Im-4 + 5*) are found only in C₁-PIM-Cl (the top curve in Figure 2(A)) at 10.67 and 7.72 ppm, respectively. Proton signals associated with the Cl-(CH₂)₃-group are shifted from 0.62, 1.78, and 3.49 ppm in the precursor P(DMS-*co*-CMS) (the mid curve in Figure 2(A); signals *a*, *b*, and *c*) to 0.51, 1.91, and 4.32 ppm in C₁-

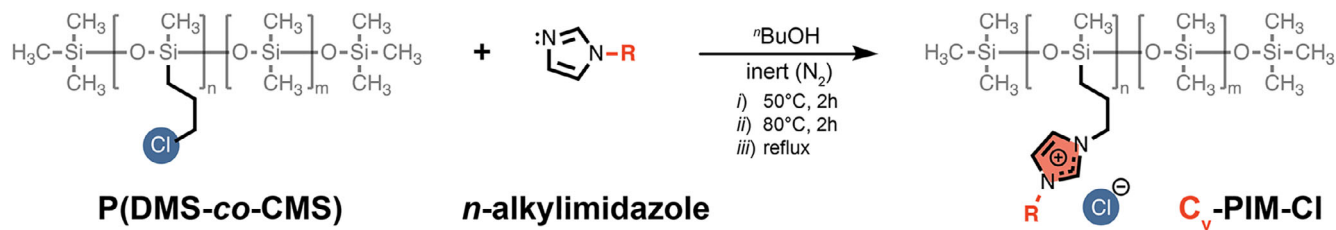


FIGURE 1 General synthetic approach towards a polysiloxane-based copolymer of PDMS and an imidazolium-type PIL. R is methyl or butyl substituent

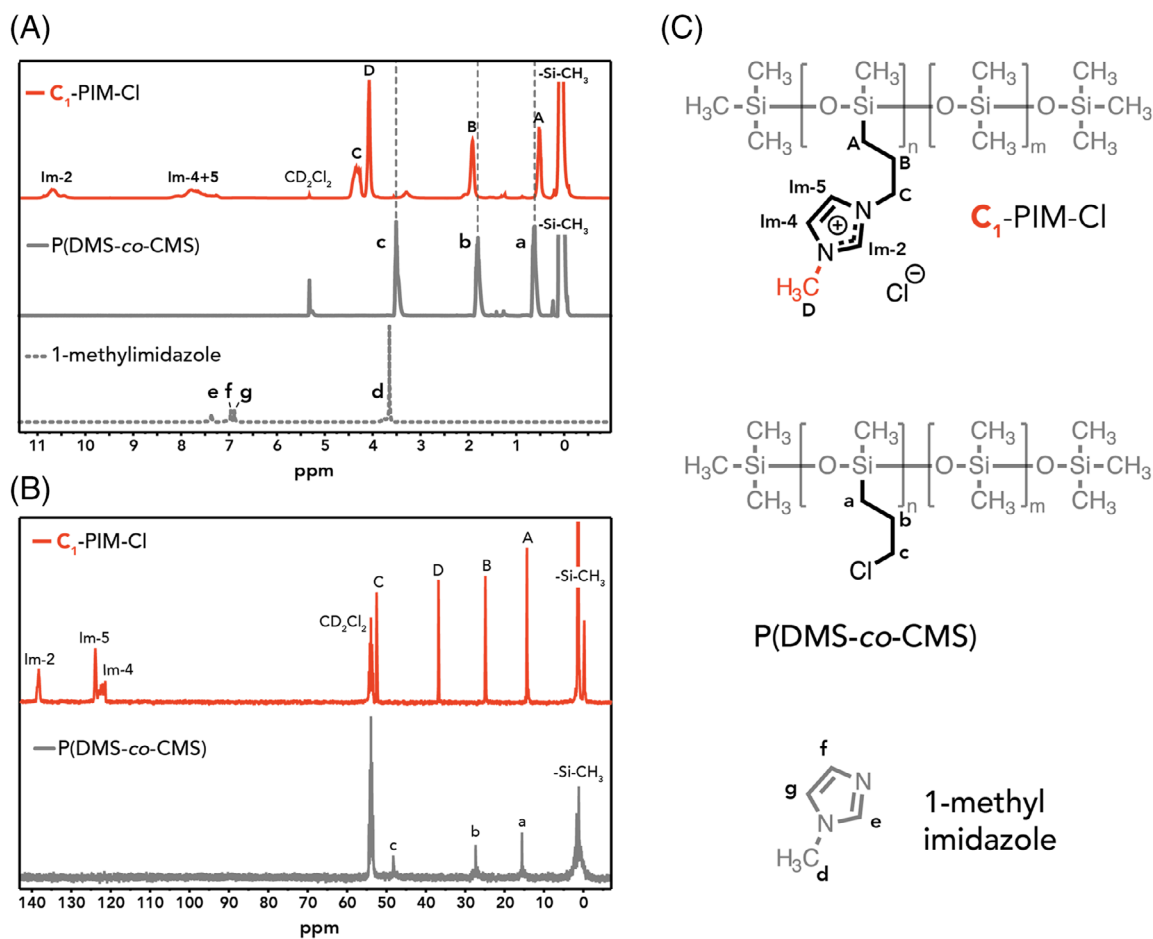


FIGURE 2 ^1H - (A) and ^{13}C -NMR (B) spectra of C_1 -PIM-Cl and its precursors recorded at 400 and 101 MHz, respectively, in CD_2Cl_2 . (C) Chemical structures with signals being labeled

PIM-Cl (the top curve in Figure 2(A); signals A, B, and C). The same occurs to the CH_3 -group on the imidazolium ring when comparing 1-methylimidazole (the bottom curve in Figure 2(A); signal d) to C_1 -PIM-Cl (the top curve in Figure 2(A); signal D). Clearly, signals in the product are at different chemical shifts than in the starting materials, which underline a quantitative conversion of all chloropropyl units into dialkylimidazolium cations. The signal around 0.06 ppm is assigned to the $-\text{Si}-\text{CH}_3$ protons. The ^{13}C -NMR spectra of C_1 -PIM-Cl and the precursor P(DMS-co-CMS) are shown in Figure 2(B).

The product spectrum (the top curve in Figure 2(B)) reveals signals associated with the imidazolium ring (*Im-2* and *Im-4 + 5*) at 138.6 and 124.1 ppm, respectively, thereby confirming its presence in the ionic copolymer. These signals are fully absent in the spectrum of the precursor P(DMS-co-CMS) (the bottom curve in Figure 2(B)). In addition, the small shoulder peak at 0 ppm is assigned to the $-\text{Si}-\text{CH}_3$ species at the chain end. The chemical structures of both the precursors P(DMS-co-CMS) and 1-methylimidazole, and the product C_1 -PIM-Cl are shown in Figure 2(C).

The formation of the imidazolium cation was also underlined by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, as shown in Figure 3. The combinational vibration of N-CH/N-CH₂/N-CH₃ stretching, typical for aromatic imidazolium rings, is observed in the spectrum of the product C₁-PIM-Cl around 1170 cm⁻¹ (the top curve in Figure 3).^{23–25} This signal is absent in the spectrum of the precursor P(DMS-co-CMS) (the bottom curve in Figure 3). All characteristic siloxane-type bands found in the starting material are also present in the product, for example, ν (Si-CH₃) \approx 1256, 856, and 792 cm⁻¹, as well as ν (Si-O-Si) \approx 1057 and 1008 cm⁻¹.²⁶ It is worth noting that the spectrum is dominated by Si-(CH₃)_x bands, and therefore modes corresponding to C-Cl groups are not detectable. Overall, these data confirmed the formation of imidazolium rings and the high purity of the product.

The molar content of the quaternized repeat unit in C₁-PIM-Cl was calculated to be 24 mol% from the ¹H-NMR spectrum (cf. ESI, Figure S2). To our surprise, this value is higher than the 14.8 mol% of the (chloropropyl) methylsiloxane repeat unit in the neutral P(DMS-co-CMS), determined by ¹H-NMR spectroscopy (cf. ESI, Figure S2). Such difference is presumably caused by the purification procedure, during which the polar reaction mixture was precipitated into diethyl ether. Only the oily precipitate (the imidazolium-rich polymer fraction) was collected, while the soluble or dispersible imidazolium-poor polymer fraction was removed. Note that the values for the molar content of quaternized repeat units given above are the average values obtained from ¹H-NMR spectroscopy, that is, the samples of product and

precursor may comprise a mixture of polymer chains with different imidazolium contents.

The polymeric nature of C₁-PIM-Cl was confirmed by size-exclusion chromatography (SEC) in aqueous medium. The apparent average molecular weight is $M_n = 25.6$ kDa ($M_w = 78.5$ kDa) with a dispersity of 3.07 (Figure S3). The reference SEC measurement of the precursor P(DMS-co-CMS) performed in THF as eluent showed a $M_n = 11.7$ kDa ($M_w = 22.8$ kDa). These values are not to be compared directly due to different calibration standards in different SEC systems, but prove the polymeric nature of our samples and the polydispersity index of the molecular weight of these polymers.

Differential scanning calorimetry (DSC) measurements were performed in order to characterize the thermal properties of C₁-PIM-Cl, including its T_g . All measurements were conducted in a temperature range of -160 to 100°C under nitrogen flow. Generally speaking, the shape of DSC curves and consequently the thermal characteristics are affected by the heating/cooling rates.^{27,28} We used a heating rate of 20°C/min for all DSC measurements as it provided the most distinctive T_g (Figure S4). Figure 4 shows the DSC traces of C₁-PIM-Cl measured under these conditions (orange). For reasons of comparison, the starting material P(DMS-co-CMS) is depicted as well (gray). In addition, Figure 4 shows the cooling traces prior to heating. C₁-PIM-Cl exhibits a T_g of -49°C, which we calculated as local maximum of the first order derivative of heat flow. This value already represents an unusually low T_g for a Cl⁻-containing PIL copolymer, as chloride ions are known to associate strongly with imidazolium cations due to their point charge character. Typically, this leads to high T_g s, as for instance in imidazolium-type polystyrene²⁹ ($T_g = 180^\circ\text{C}$).

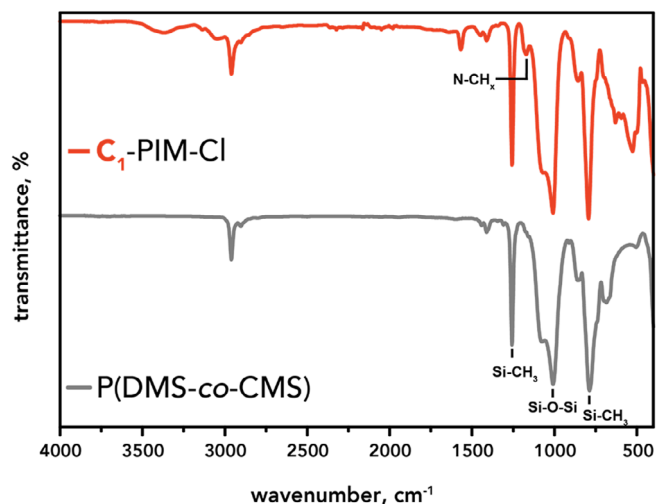


FIGURE 3 ATR-FTIR spectra of C₁-PIM-cl and P(DMS-co-CMS). Transmittance was recalculated on basis of reflection. Modes characteristic for imidazolium and polysiloxane are labeled

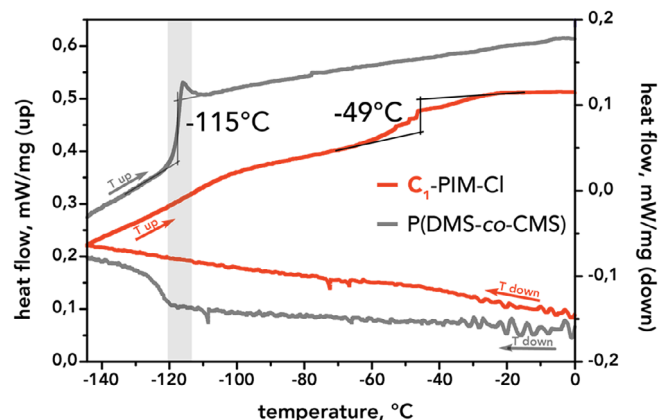


FIGURE 4 DSC heating (20°C/min) and cooling traces (10°C/min) for C₁-PIM-cl and the precursor P(DMS-co-CMS). T_g was calculated as local maximum of first order derivative of heat flow

The fact that our product C₁-PIM-Cl shows a significantly lower T_g is rooted in the flexible nature of the polysiloxane backbone.^{11,17} Surprisingly, the DSC trace of C₁-PIM-Cl reveals a second, less pronounced phase transition at -110°C (Figure S5), which is characteristic for polysiloxanes,¹⁶ as observed in the precursor P(DMS-co-CMS). We assume that this weak T_g is caused by a PDMS-rich microphase in the product C₁-PIM-Cl, especially since dimethylsiloxane repeat units account for 76 mol% within the copolymer. Microphase separation is a phenomenon generally found in block copolymers carrying incompatible blocks.^{6,30} Depending on the composition, such materials might exhibit individual glass transitions for each block.^{31,32} Though not common, random copolymers are also capable of microphase separation, as theoretically predicted^{33,34} and experimentally underlined.^{35–39} It is important to note that, although we refer to our siloxane-based precursor as a supposedly randomly distributed copolymer, we cannot rule out compositional gradients within this commercial system, which might have a dramatic effect on its phase properties.

Based on the results presented so far, we have shown that the combination of a highly flexible PDMS backbone with pendant imidazolium chloride ion pairs presents a simple strategy towards low- T_g ionic copolymers. It is worth noting that, among many other factors, a low T_g can lead to very high ionic conductivities in PILs.^{11,40} In the following section we describe the optimization of the chemical structure of our PIL-based copolymers towards further lowering down its T_g and ultimately promoting the ionic conduction behavior.

2.2 | Optimization of the chemical structure

In general, there are three strategies to alter the chemical structure of our copolymer C₁-PIM-Cl, which can be exploited towards achieving a lower T_g : (a) Exchanging the Cl[−] with a bulkier anion; (b) Introducing long spacers between the backbone and the cation to increase the mobility of the ionic species; (c) Attaching alkyl chains of optimized length to imidazolium and thereby plasticizing the polymer matrix. All these approaches are well known to dramatically affect the properties of PILs, in particular the glass transition.^{40–43} We carried out a new set of experiments with the same precursor, and followed the above-described approaches (a) and (c) in order to find the lowest possible T_g .

First, we exchanged chloride ions in C₁-PIM-Cl with TFSI[−], PF₆[−], and BF₄[−], respectively, through anion metathesis. Thereby, we were able to determine the anion with the strongest impact on T_g . Second, we

replaced the methyl group attached to the imidazolium ring with a longer alkyl chain, specifically with *n*-butyl, and then exchanged Cl[−] by the anion-of-choice (as determined through our first set of experiments). This allowed us to approach the lowest possible T_g .

2.2.1 | Anion metathesis reactions

Anion metathesis reactions were performed with AgX salts (with X denoting TFSI[−], PF₆[−], or BF₄[−]) to assist the anion exchange.⁴¹ In a typical experiment, 1 eq. of C₁-PIM-Cl was dissolved in ethanol and, while stirring, a slight excess of dissolved silver salt was added (see Exp. section for details). The anion-exchanged products C₁-PIM-X (with X denoting TFSI[−], PF₆[−], or BF₄[−]) remain soluble, despite being more hydrophobic than the chloride containing C₁-PIM-Cl. After removal of silver chloride, the samples were isolated and purified. The absence of chloride in the anion-exchanged products was confirmed by titrating C₁-PIM-X against silver nitrate. The fact that no silver chloride precipitate was found allowed us to conclude that the previous anion metatheses had been completed. All anion-exchanged products visibly showed a lower viscosity than their precursor C₁-PIM-Cl at room temperature. Compared to C₁-PIM-Cl, which is soluble in water (see Table S1), the anion-exchanged products are not, given their increasingly more hydrophobic anions. Independent of the types of anions used, both ¹H- and ¹³C-NMR spectra (Figure S6) remained similar to that of C₁-PIM-Cl. No additional signals compared to C₁-PIM-Cl were observed in the ¹H-NMR spectra of C₁-PIM-TFSI, C₁-PIM-PF₆, and C₁-PIM-BF₄, respectively, which was expected since TFSI[−], PF₆[−], and BF₄[−] are free of hydrogen atoms. Yet, new peaks associated with TFSI[−] (CF₃-group) appeared in the ¹³C-NMR spectrum of C₁-PIM-TFSI. ATR-FTIR spectroscopy confirmed the successful anion exchange by the presence of stretching modes characteristic for TFSI[−], for example, $\nu_{\text{as}}^-(\text{SO}_2) \approx 1349 \text{ cm}^{-1}$, $\nu_{\text{as}}^-(\text{CF}_3) \approx 1186 \text{ cm}^{-1}$, and $\nu_{\text{s}}^-(\text{SO}_2) \approx 1135 \text{ cm}^{-1}$,^{44,45} as well as for PF₆[−], for example, $\nu_{\text{s}}^-(\text{P-F}) \approx 820 \text{ cm}^{-1}$,⁴⁶ see Figure S6.

We then performed DSC measurements to study the impact of anion exchange on T_g . Figure 5(A) depicts the heating curves for all C₁-PIM-X polymers, plus the curve of the precursor P(DMS-co-CMS). Clearly, the choice of anion strongly affects the glass transition. For example, C₁-PIM-TFSI exhibits a T_g of -67°C . Surprisingly, both C₁-PIM-BF₄ and C₁-PIM-PF₆ reveal significantly higher T_g s of -47 and -32°C , respectively. These values are even higher than the one for C₁-PIM-Cl. This is somewhat counter-intuitive, considering the fact that both PF₆[−]- and BF₄[−]-ions have lower coordination

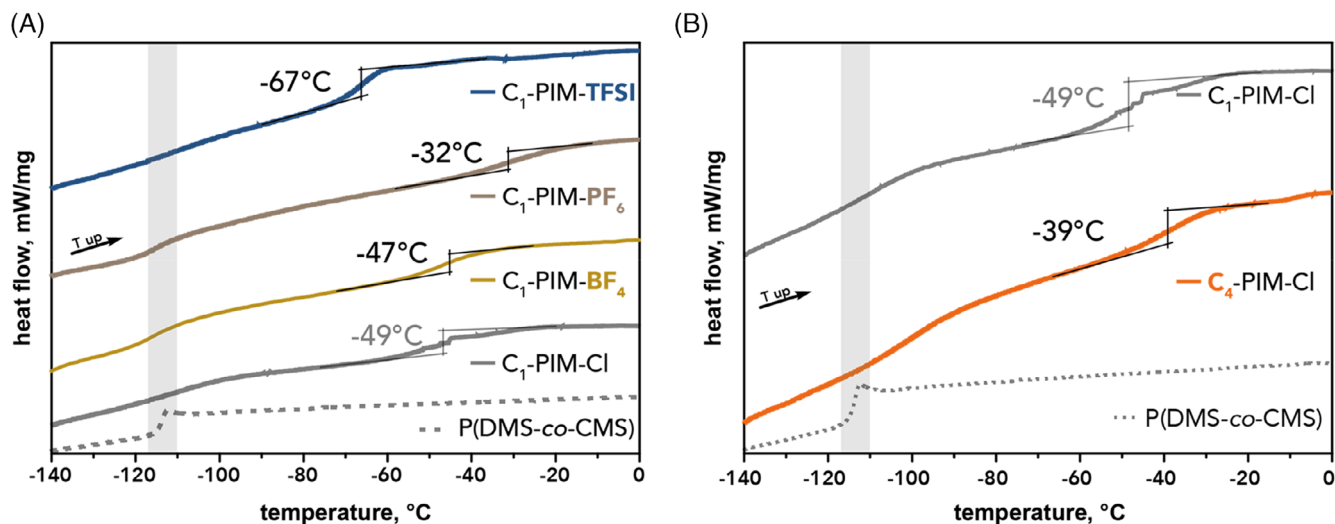


FIGURE 5 (A, B) DSC heating traces for C_1 -PIM-X and C_y -PIM-cl ($X = \text{cl, TFSI, PF}_6, \text{ or BF}_4$ anion, $y = 1, 4$), respectively. Heating curves were obtained at a heating rate of $20^\circ\text{C}/\text{min}$. T_g values are indicated next to the curves and were calculated as local maxima of first order derivative of heat flow

tendencies towards the imidazolium cation than chloride.⁴⁷ To our surprise, the DSC trace of C_1 -PIM-TFSI revealed only one phase transition. It seems that the presence of the more hydrophobic TFSI⁻ anion improves the compatibility between the ion-rich and the ion-poor domains within the copolymer. This is in stark contrast to C_1 -PIM-Cl, which showed an additional T_g at -110°C . Also, both C_1 -PIM-BF₄ and C_1 -PIM-PF₆ revealed a clear second phase transition in the same region. As discussed earlier, we attributed this phenomenon to the PDMS-rich microdomains, which we hypothesize to be phase-separated from the ion cluster domains in the copolymer.

Overall, the introduction of bulky, weakly coordinating anions (TFSI⁻, PF₆⁻, and BF₄⁻) provides a simple means to tune the properties of PILs, in particular their thermal properties. We found the strongest effect for TFSI⁻. Next, we focused on replacing the methyl group attached to the imidazolium cation by a longer alkyl chain.

2.2.2 | Tuning the length

Tuning the length of the alkyl chain attached to the imidazolium cation, and thereby replacing the methyl group for a longer alkyl substituent, is a simple way to modify T_g of our copolymer product. On the one hand, a longer alkyl chain will increase the size of the cation and eventually weaken its interaction with the anion; on the other hand, it can also amplify the hydrophobic interactions, and very long alkyl chains could even crystallize at

room temperature. We followed a similar synthetic route as earlier, but utilized *n*-butylimidazole as a starting compound. Thereby, we prepared a new ionic copolymer with a longer alkyl chain and were able to study its impact on T_g . As expected, the use of *n*-butylimidazole engendered an increase in reaction time to reach a full conversion and the resulting ionic copolymer became increasingly more hydrophobic. The formation of imidazolium rings was confirmed by ¹H- and ¹³C-NMR spectroscopy (Figures S8 and S9). The molar ratio of quaternized repeat unit was calculated as 21% and thus was similar to the one in C_1 -PIM-Cl (24%).

The successful formation of imidazolium chloride ion pairs was underlined by ATR-FTIR-spectroscopy. The characteristic modes related to both imidazolium and PDMS, as similarly discussed earlier, are present in C_4 -PIM-Cl. The resulting ionic copolymer exhibited increased viscosity, which points out stronger hydrophobic interactions. The corresponding DSC measurement is depicted in Figure 5(B) (cf. Figure S10 for the cooling period) and clearly shows that T_g shifts from -49 to -39°C upon replacing the short methyl with the longer *n*-butyl moiety. Still, the sample exhibits a relatively low T_g . Also, a second T_g at lower temperature was observed, similar to that in C_1 -PIM-Cl. Overall, it was indeed possible to tune T_g of the ionic copolymer by replacing the methyl group attached to the imidazolium cation with a longer alkyl substituent. However, we did not observe the desired decrease in T_g . At the same time, we demonstrated the versatility of our synthetic approach.

2.3 | Structure synergy and conductivity

As evident from the previous section, the use of both the TFSI⁻-anions and short alkyl substituents (in particular methyl) favors a low T_g . Yet, C₄-PIM-Cl showed relatively low T_g of -39°C . Hence, we became interested in combining this copolymer with TFSI⁻-anions too, in order to assess whether we could achieve a comparably low T_g as the combination of methyl and TFSI⁻ in C₁-PIM-TFSI. Consequently, we prepared C₄-PIM-TFSI by anion metathesis of C₄-PIM-Cl with AgTFSI. The ¹H- and ¹³C-NMR, as well as the ATR-FTIR spectra (cf. Figure S11) confirmed its chemical structure. Most excitingly, the DSC trace (Figure 6(A), cf. Figure S12) revealed a T_g at -73°C for C₄-PIM-TFSI, which is the lowest T_g ever reported for an imidazolium-based PIL homo- or copolymer.^{42,48} Previous records of low- T_g polyimidazoliums include Choi's^{42,48} radically polymerized imidazolium acrylates (-47°C), and Jourdain's¹¹ siloxane-based poly(1,2,3-triazolium) PIL (-62°C). It is worth noting, that C₄-PIM-TFSI exhibits a slightly higher T_g than Liang's¹⁷ phosphonium-based polysiloxanes.

Clearly, C₄-PIM-TFSI reveals a slightly lower T_g (-73°C) than its shorter homologue C₁-PIM-TFSI (-67°C). We previously mentioned that a longer alkyl chain promotes hydrophobic interactions. Here, the presence of the bulky and shape-anisotropic TFSI⁻-anion manifests in a plasticizing effect, which is more dominant than the hydrophobic interactions. This agrees with a recent report by Choi⁴⁸ and coworkers, in which they managed a lower T_g of imidazolium-based polyacrylates by increasing the side-chain length to a certain extent. The authors used TFSI⁻ and PF₆⁻ as anions and

attributed the lower T_g to an increasing size of charged repeat units.^{42,43} In another article, they observed this trend independent of the types of anions used,⁴⁹ which is different from our findings here, as we noticed a strong dependence of T_g on the choice of anions in the current polysiloxane imidazolium system.

It is generally accepted that a low T_g is crucial to achieve high ionic conductivities in PILs.¹¹ C₄-PIM-TFSI showed the lowest T_g of all imidazolium-based PILs and is thus promising as ion conducting material. In order to determine its anhydrous (water-free) temperature-dependent direct current (DC) conductivity (σ_{DC}), broadband dielectric spectroscopy (BDS) was employed. Since the anion exchange strongly affects T_g , the ionic conductivity is expected to follow a similar trend. To underline this assumption, BDS measurements were also conducted with C₄-PIM-Cl. Measurements were carried out in a temperature range from 160 to 480 K and in a frequency window between 10^{-2} and 10^{+7} Hz. The values of σ_{DC} were derived from the distinct plateaus in the spectra of the real part of the complex conductivity (cf. Figures S13, S14, and S15).

Figure 6(B) reveals the ionic conductivity of both samples against reciprocal temperature. The temperature dependence of σ_{DC} follows a Vogel-Fulcher-Tammann (VFT) relation above T_g . A dotted line in Figure 6(B) represents 300 K, where C₄-PIM-Cl showed an ionic conductivity of 2.5×10^{-7} S/cm. This is relatively high for a halide-containing polyimidazolium. Usually, PILs carrying imidazolium chloride ion pairs show considerably lower values around 10^{-10} S/cm.² Excitingly, C₄-PIM-TFSI revealed a DC-conductivity of 4.8×10^{-5} S/cm. This is among the highest values ever reported for PILs.^{11,50} Precisely

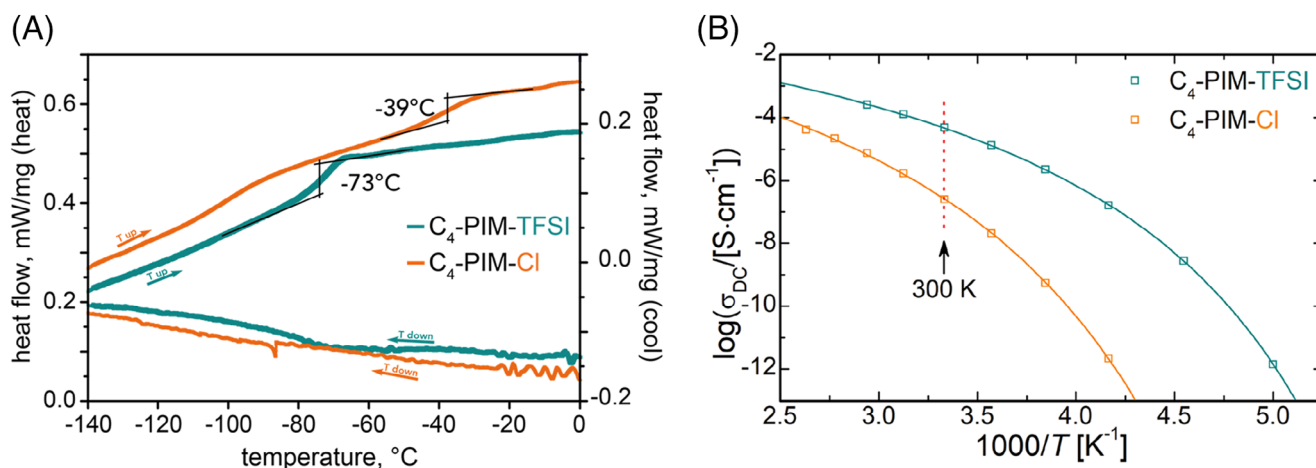


FIGURE 6 (A) DSC traces of C₄-PIM-TFSI and C₄-PIM-cl. (B) Temperature-dependent direct current (DC) conductivity (σ_{DC}) obtained from BDS measurements through fitting the Dyre formula^{51,52} to the distinct plateau and the AC conductivity contribution to the real part of the complex conductivity spectra. Curves were fitted with a Vogel-Fulcher-Tammann (VFT) dependence

speaking, to the best of our knowledge, this is the highest DC-conductivity of any imidazolium-based PIL so far.^{2,19} As an example, our polymer exceeds the recent work by Karlsson, who pursued a similar strategy, that is, starting from the same precursor and using “click-chemistry” to obtain PILs ($\sim 2 \times 10^{-5}$ S/cm).¹⁹ Among other poly-cations, the conductivity of our polymer is comparable to Frenzel's⁵⁰ sulfonium-based polyacrylate containing bulky ammonium ions ($3\text{--}6 \times 10^{-5}$ S/cm depending on molecular weight). However, Jourdain and coworkers recently reported an even higher ion conductivity for their 1,2,3-triazolium-based polysiloxane ($\sim 6.7 \times 10^{-5}$ S/cm).¹¹

In addition to the plateau of the DC conductivity contribution in the real conductivity spectra (σ'), the conductivity functions of both samples C₄-PIM-Cl and C₄-PIM-TFSI exhibit a shoulder at lower frequencies. The temperature-dependent frequency of this shoulder and the strength of the dielectric permittivity at this particular frequency suggest that it arises from polarization within the sample distinct from polarization at the sample-electrode interface.⁵² Thus, this observation strongly indicates that the samples might undergo microscopic phase separation as discussed above.

3 | CONCLUSIONS

With this contribution, we present a simple synthetic route towards siloxane-based PILs with pendant imidazolium-type IL-like species. We expanded the scope of our system towards an unusually low T_g by introducing bulky anions and alkyl substituents of short and intermediate length. As a result, we obtained an imidazolium-containing copolymer with a record-low T_g of -73°C . Such a low T_g is a consequence of (a) the flexible polysiloxane backbone,¹¹ (b) the propyl spacer separating charges from the backbone,² (c) the low coordination tendency of TFSI⁻ with the cation and its action as a plasticizer,⁴⁹ and (d) the increasing mobility of the repeat unit due to longer alkyl substituents, which reduces the cation-anion association.^{42,43} At the same time, our product exhibits a strikingly high DC-conductivity of 4.8×10^{-5} S/cm at 300 K, elevating our novel PIL to one of the highest conducting ionic polymers so far.^{11,19,50}

4 | EXPERIMENTAL SECTION/ METHODS

4.1 | Substitution with 1-(*n*-alkyl)imidazole

In a typical experiment, the precursor P(DMS-*co*-CMS) was weighed into a three-necked round-bottom flask

equipped with a reflux condenser. The apparatus was schlenked using nitrogen and the precursor dissolved in *n*-butanol (degassed prior to use). Subsequently, the corresponding 1-(*n*-alkyl)imidazole (20 mol eq. per Cl) was added via a syringe. The clear mixture was stirred at 50°C for 2 h, at 80°C for another 2 h, and finally refluxed (i.e., $117\text{--}118^\circ\text{C}$) overnight during which the solution turned yellowish. Reaction progress was determined by ¹H-NMR spectroscopy. The reaction mixtures were centrifuged and filtered to remove any insoluble substances, and finally concentrated at 80°C under reduced pressure. The yellowish phase was dissolved in dichloromethane and subsequently precipitated into diethyl ether. The supernatant was discarded and the oily phase was washed three times with diethyl ether. This process was repeated at least three times. Finally, all samples were dried at 80°C under high vacuum (10^{-3} mbar) for 24 h, which gave almost colorless, clear, and viscous polymers.

4.2 | Anion exchange

1.0 eq. of C_{*y*}-PIM-Cl (*y* = 1, 4) was dissolved in ethanol and, while stirring, a slight excess (1.03–1.31 eq.) of dissolved silver salt (AgX with X = TFSI⁻, PF₆⁻, or BF₄⁻) was added at once under light protection. Immediate precipitation of silver chloride took place and stirring was continued at room temperature in the dark for 12 h. Subsequently, the mixture was centrifuged and the supernatant was collected. The precipitate was washed with ethanol and centrifuged again. The combined supernatants were filtered and concentrated at 80°C under reduced pressure. In case of C₁-PIM-PF₆ and C₁-PIM-BF₄, the crude products were washed with dichloromethane three times. C₁-PIM-TFSI was dialyzed in ethanol for 2 days (membrane with molecular weight cut-off of 3.5 kDa). Finally, all products were dried at 80°C under high-vacuum (10^{-3} mbar) for 24 h to yield clear and viscous polymers. The absence of Cl⁻ ions in all samples was confirmed by silver nitrate titration.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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