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Synthesis of Pyrrolidinium-Based Poly(ionic liquid) Electrolytes with Poly(ethylene glycol) Side Chains

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S *Supporting Information*

ABSTRACT: The synthesis and characterization of a new family of pyrrolidinium based poly(ionic liquid) (PIL) electrolytes with poly-(ethylene glycol) (PEG) pendant groups is reported. The PILs were synthesized from a diallyl methyl amine hydrochloride monomer, which was obtained in large quantities using a modified Eschweiler-Clarke reaction. As additional plasticizers for the PILs, pyrrolidinium ionic liquids (ILs), also with PEG groups, were synthesized. All obtained PILs and ILs revealed excellent thermal stabilities to greater than 300 °C. Binary electrolyte mixtures were prepared by blending the PILs and ILs in different weight ratios. In addition, a ternary mixture of the best performing PIL and IL and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) was prepared. The obtained electrolyte blends showed very good ionic conductivities in the best case up to 2.4 mS cm^{-1} at 25 °C and 10.2 mS cm^{-1} at 100 °C and outperformed their pyrrolidinium counterparts with alkyl side chain that were synthesized as a reference. It was found that the ionic conductivity of the blends increased with an increase in the PEG chain length of the PILs. The good physicochemical properties of the presented materials make them potential candidates for electrochemical applications such as lithium-ion batteries or dye-sensitized solar cells.

KEYWORDS: *poly(ionic liquid), ionic liquid, pyrrolidinium, poly(ethylene glycol), polymer electrolyte*
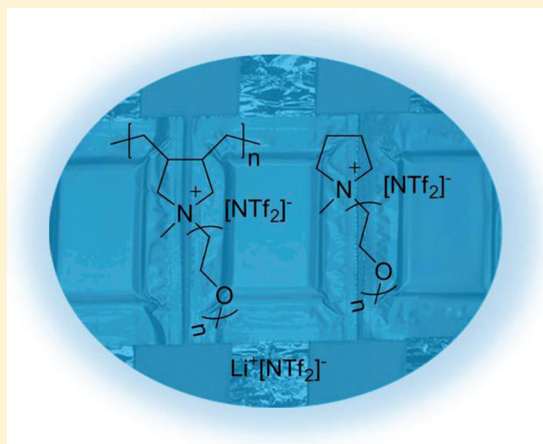
1. INTRODUCTION

The synthesis of solvent-free electrolyte materials for sustainable electrochemical applications such as lithium-ion batteries, solar-cells, electrochromic windows, supercapacitors etc., with excellent physicochemical properties, i.e., thermal and electrochemical stability, high ionic conductivity, nonvolatility and a high viscosity to suppress leakage, is a topic of current interest. Among these new electrolytes, ionic liquids (ILs) and poly(ionic liquid)s (PILs) represent an important class of materials as they can exceed the stability and performance of electrochemical devices made with conventional, organic solvent-based electrolytes.[1,2] This clear advantage has very recently led to several studies that described the synthesis and characterization of several new IL-based electrolytes. For example, the synthesis of poly(ethylene glycol) (PEG) functionalized imidazolium ionic liquids was reported.[3] It was found that the developed ionic liquids with long PEG side chains exhibited conductivities in the order of 0.1 mS cm^{-1} despite their relatively high viscosities. In another study, the phase behavior of pyrrolidinium ionic liquid/lithium salt mixtures was evaluated in order to understand the processes that occur in the electrolytes to finally optimize their ionic conductivity.[4] Another work described the synthesis of pyrrolidinium-based ILs with ether groups which were used as plasticizers for polyethylene oxide to obtain stable electrolyte membranes with very good performances.[5] A further work reported on the synthesis of anionic poly(ionic liquid)s with dialkylpyrrolidinium counter cations with a high charge delocalization.[6] In a recent article, an overview of the latest developments in the lithium-ion battery technology was reported with particular attention to pyrrolidinium ILs as an interesting and safe electrolyte media for advanced batteries.[7] These examples highlight the importance of ionic liquids and their derivatives for the development of new electrolyte materials.

Whereas extensive research has been devoted to novel imidazolium-based poly(ionic liquid)s and electrolytes,[2,8−13] the development of pyrrolidinium-based materials, and

especially polymers, has not been fully explored yet. Even though, pyrrolidinium is known to possess a better electrochemical stability than imidazolium because of its nonaromatic character, which can be beneficial for electrochemical applications.[14,15]

This article reports on the synthesis and characterization of a new class of pyrrolidinium-based poly(ionic liquid) electrolytes. This was achieved by starting from a diallyl methyl amine hydrochloride monomer, which was prepared in large quantities using a modified Eschweiler-Clarke reaction. The corresponding polymer was obtained by free radical polymerization, then neutralized and subsequently modified with PEG side chains of different lengths by quaternization reactions. In addition, several pyrrolidinium ILs with PEG groups were synthesized and used as plasticizers for these new polymer electrolytes. All materials revealed excellent thermal stabilities and very good ionic conductivities, making them suitable for being applied in a wide range of electrochemical devices.

2. EXPERIMENTAL SECTION

2.1. Materials. Diallylamine (99%), formaldehyde solution (37 wt. % in H$_2$O), formic acid (98%), p-toluenesulfonyl chloride (≥98%), 2-methoxyethanol (99.8%), 2-(2-methoxyethoxy)ethanol (≥99.0%), 2-(2-(2-metoxyethoxy)ethoxy)ethanol (≥97.0%), potassium carbonate (≥99.0%), sodium methoxide solution (25 wt.% in methanol), sodium iodide (≥99.0%), 1-methylpyrrolidine (≥99.0%), bis-(trifluoromethane)sulfonimide lithium salt (≥99.0%) and silver nitrate solution (1.0 N in H$_2$O) were purchased from Aldrich. 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (98%), hydrochloric acid (37 wt.% in H$_2$O), N,N-dimethylformamide (DMF, 99.0%), toluene (99.5%), diethyl ether (99.5%), ethanol (≥99.8%) and acetone (99.5%) were purchased from Scharlab. 1-Butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide (PYR$_{14}$TFSI) was provided by Solvionic. All chemicals were used as received. Bis(trifluoromethane)-sulfonimide lithium salt was dried under vacuum at 120 °C for 24 h before use.

2.2. Synthesis of Diallyl Methyl Amine Hydrochloride. The product was obtained using a modified Eschweiler-Clarke reaction.[16,17] Diallylamine (1 equiv., 0.45 mol, 43.7 g) was slowly added to a solution of formic acid (5.3 equiv., 2.38 mol, 122 g) cooled to 0 °C in a 500 mL round-bottom flask. To the resulting clear solution a formaldehyde solution (37% solution; 1.5 equiv., 0.675 mol, 55 g) was added and the mixture was stirred at room temperature for 1 h (evolution of carbon dioxide). After this time, the flask was connected to a reflux condenser and the reaction mixture was heated overnight at 100 °C. After, the solution was cooled and aqueous HCl (4 N, 2 equiv., 0.9 mol, 225 mL) was added. The crude reaction was evaporated to dryness under reduced pressure. ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.95 (m, 2H, NCH$_2$CHCH$_2$), 5.62 (m, 4H, NCH$_2$CHCH$_2$), 3.77 (d, 4H, J = 7.0 Hz, NCH$_2$CHCH$_2$), 2.82 (s, 3H, NCH$_3$).

2.3. General Procedure for the Tosylation of Primary Alcohols. The products were obtained by adapting literature procedures.[18] A mortar was charged with the alcohol (1.2 equiv.), K$_2$CO$_3$ (4 equiv.), and p-toluenesulfonyl chloride (1.0 equiv.), and grinded vigorously for 10 min and allowed to set for another 10 min. The reaction was followed by TLC (hexane) until total consumption of tosyl chloride was observed. The product was extracted with diethyl ether and filtered. The organic layer was washed with water and KHCO$_3$ (sat. solution) and dried over MgSO$_4$. The solvent was evaporated under reduced pressure.

2.3.1. (2-Methoxy)ethyl p-toluenesulfonate. The general procedure was followed starting from 2-methoxyethanol (90 mmol, 6.84 g), K$_2$CO$_3$ (300 mmol, 41.46 g) and p-toluenesulfonyl chloride (75 mmol, 14.25 g). Clear liquid. Yield: 16.35 g (95%).^{1}H NMR (500 MHz, CDCl$_3$): δ 7.8 (d, 2H, J = 8.2 Hz, Ph), 7.35 (d, 2H, J = 8.1 Hz, Ph), 4.16 (t, 2H, J = 4.7 Hz, CH$_2$OTs), 3.58 (t, 2H, J = 4.8 Hz, OCH$_2$CH$_2$OTs), 3.30 (s, 3H, OCH$_3$), 2.45 (s, 3H, PhCH$_3$).

2.3.2. 2-(2-Methoxyethoxy)ethyl p-toluenesulfonate. The general procedure was followed starting from 2-(2-methoxyethoxy)ethanol (90 mmol, 10.8 g), K$_2$CO$_3$ (300 mmol, 41.46 g) and p-toluenesulfonyl chloride (75 mmol, 14.25 g). Clear liquid. Yield: 19.32 g (94%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.78 (d, 2H, J = 8.3 Hz, Ph), 7.32 (d, 2H, J = 8.0 Hz, Ph), 4.16 (t, 2H, J = 4.8 Hz, CH$_2$OTs), 3.68 (t, 2H, J = 4.8 Hz, OCH$_2$CH$_2$OTs), 3.57–3.56 (m, 2H, OCH$_2$CH$_2$O), 3.47–3.46 (m, 2H, OCH$_2$CH$_2$O), 3.30 (s, 3H, OCH$_3$), 2.43 (s, 3H, PhCH$_3$).

2.3.3. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl p-toluenesulfonate. The general procedure was followed starting from 2-(2-(2-methoxyethoxy)ethoxy)ethanol (90 mmol, 14.78 g), K$_2$CO$_3$ (300 mmol, 41.46 g) and p-toluenesulfonyl chloride (75 mmol, 14.25 g). Clear liquid. Yield: 19.125 g (66%).^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 (d, 2H, J = 8.3 Hz, Ph), 7.31 (d, 2H, J = 8.0 Hz, Ph), 4.13 (t, 2H, J = 4.9 Hz, CH$_2$OTs), 3.65 (t, 2H, J = 4.8 Hz, OCH$_2$CH$_2$OTs), 3.61–3.55 (m, 6H, OCH$_2$CH$_2$O), 3.50–3.48 (m, 2H, OCH$_2$CH$_2$O), 3.33 (s, 3H, OCH$_3$), 2.41 (s, 3H, PhCH$_3$).

2.4. General Procedure for Iodination. The products were obtained following literature procedures.[19] The p-toluenesulfonate derivatives (1 equiv.) were dissolved in acetone and sodium iodide (1.2 equiv.) was added. The reaction mixtures were stirred at room temperature under nitrogen in the dark for 24 h. The reaction mixtures were filtered and the solvent removed under reduced pressure. The products were purified by flash chromatography.

2.4.1. (2-Methoxyethoxy)ethyl Iodide. General procedure was followed starting from (2-methoxy)ethyl p-toluenesulfonate (60 mmol, 13.82 g) and NaI (72 mmol, 10.79 g) in acetone (150 mL). Yellowish liquid. Yield: 10.60 g (95%). ^{1}H NMR (500 MHz, CDCl3): δ 3.64 (t, 2H, J = 6.6 Hz, OCH$_2$), 3.39 (s, 3H, OCH$_3$), 3.25 (t, 2H, J = 6.7 Hz, CH$_2$I).

2.4.2. 2-(2-Methoxyethoxy)ethyl Iodide. General procedure was followed starting from 2-(2-methoxyethoxy)ethyl p-toluenesulfonate (60 mmol, 16.46 g) and NaI (72 mmol, 10.79 g) in acetone (150 mL). Yellowish liquid. Yield: 12.84 g (93%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.73 (t, 2H, J = 6.7 Hz, OCH$_2$CH$_2$I), 3.64–3.62 (m, 2H, OCH$_2$CH$_2$O), 3.54–3.52 (m, 2H, OCH$_2$CH$_2$O), 3.37 (s, 3H, OCH$_3$), 3.24 (t, 2H, J = 6.8 Hz, CH$_2$I).

2.4.3. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl Iodide. General procedure was followed starting from 2-(2-(2-methoxyethoxy)ethoxy)ethyl p-toluenesulfonate (60 mmol, 19.10 g) and NaI (72 mmol, 10.79 g) in acetone (150 mL). Yellowish liquid. Yield: 14.80 g (90%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.73 (t, 2H, J = 6.8 Hz, OCH$_2$CH$_2$I), 3.65–3.62 (m, 6H, OCH$_2$CH$_2$O), 3.54–3.52 (m, 2H, OCH$_2$CH$_2$O), 3.36 (s, 3H, OCH$_3$), 3.24 (t, 2H, J = 7.0 Hz, CH$_2$I).

2.5. Synthesis of 1-Methylpyrrolidinium-Based Ionic Liquids. The products were obtained by adapting literature procedures.[5,20] To pyrrolidine (1 equiv.) in toluene the alkyl iodides (1.2 equiv.) were added. The reaction mixtures were vigorously stirred at room temperature for 48 h. The formed iodide ionic liquids were insoluble in toluene and could be separated by decantation. The ionic liquids were washed with diethylether (3x) and residual solvent was removed under reduced pressure. The slightly yellow ionic liquids were stirred in water with activated carbon for 24 h to decolorize and then filtered. To the aqueous ionic liquid solutions (1.0 equiv.) bis(trifluoromethane)sulfonimide (LiTFSI, 1.2 equiv.) aqueous solution was slowly added. The reaction mixtures were stirred at room temperature. A phase separation was observed due to an anion exchange of the iodide by the hydrophobic TFSI anion. The ionic liquids were separated by decantation and successively washed with water several times. The aqueous phases were tested with AgNO$_3$ until all lithium iodide was removed. The ionic liquids were dried under vacuum at 120 °C for 24 h before use.

2.5.1. 1-(2-Methoxyethyl)-1-methylpyrrolidinium bis-(trifluoromethane)sulfonimide (IL2). The general procedure was followed starting from methylpyrrolidine (28 mmol, 2.38 g) and (2-methoxyethoxy)ethyl iodide (34 mmol, 6.80 g) in toluene (10 mL) to obtain the iodide ionic liquid. Yield: 6.15 g (81%). For the anion exchange, bis(trifluoromethane)sulfonimide lithium salt (24 mmol, 6.89 g) aqueous solution was slowly added to 1-(2-methoxyethyl)-1-methylpyrrolidinium iodide (5.42 g, 20 mmol) aqueous solution. Clear

liquid. Yield: 6.11 g (72%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 3.93−3.90 (m, 2H,CH_2O), 3.75−3.70 (m, 6H, NCH_2), 3.38 (s, 3H, OCH_3), 3.26 (s, 3H, NCH_3), 2.33−2.56 (m, 4H, CH_2CH_2).

2.5.2. 1-(2-(2-Methoxyethoxy)ethyl)-1-ethylpyrrolidinium bis-(trifluoromethane)sulfonimide (IL3). The general procedure was followed starting from methylpyrrolidine (28 mmol, 2.38 g) and 2-(2-methoxyethoxy)ethyl iodide (34 mmol, 7.82 g) in toluene (10 mL) to obtain the iodide ionic liquid. Yield: 6.88 g (78%). For the anion exchange, bis(trifluoromethane)sulfonimide lithium salt (24 mmol, 6.89 g) aqueous solution was slowly added to 1-(2-(2-methoxyethoxy)ethyl)-1-ethylpyrrolidinium iodide (6.30 g, 20 mmol) aqueous solution. Clear liquid. Yield: 5.90 g (63%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 4.03−4.00 (m, 2H, NCH_2CH_2O), 3.77−3.72 (m, 2H, OCH_2CH_2O), 3.68−3.66 (m, 2H, OCH_2CH_2O), 3.54−3.52 (m, 6H, NCH_2), 3.31 (s, 3H, OCH_3), 3.27 (s, 3H, NCH_3), 2.33−2.56 (m, 4H, CH_2CH_2).

2.5.3. 1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide (IL4). The general procedure was followed starting from methylpyrrolidine (28 mmol, 2.38 g) and 2-(2-(2-methoxyethoxy)ethoxy)ethyl iodide (34 mmol, 9.32 g) in toluene (10 mL) to obtain the iodide ionic liquid. Yield: 7.34 g (73%). For the anion exchange, bis(trifluoromethane)sulfonimide lithium salt (24 mmol, 6.89 g) aqueous solution was slowly added to 1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1-methylpyrrolidinium iodide (7.19 g, 20 mmol) aqueous solution. Clear liquid. Yield: 5.95 g (58%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 4.06−4.03 (m, 2H, NCH_2CH_2O), 3.77−3.73 (m, 6H, CH_2N), 3.69−3.67 (m, 2H, OCH_2CH_2O), 3.64−3.62 (m, 4H, OCH_2CH_2O), 3.59−3.58 (m, 2H, OCH_2CH_2O), 3.49−3.47 (m, 2H, OCH_2CH_2O), 3.29 (s, 3H, OCH_3), 3.28 (s, 3H, NCH_3), 2.33−2.27 (m, 4H, CH_2CH_2).

2.6. Synthesis of 1-Methylpyrrolidinium-Based Poly(ionic liquid)s. *2.6.1. Poly(diallyl methyl amine).* The monomer diallyl methyl ammonium hydrochloride (1 equiv., 102 mmol, 15 g) was dissolved in water (10 mL) and purged with nitrogen for 20 min. The inititator 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AAPH, 0.03 equiv., 3 mmol, 826 mg) was added and the mixture was purged for another 5 min. The reaction was stirred under nitrogen atmosphere at 60 °C for 72 h. Water was removed by freeze-drying to obtain poly(diallyl methyl amine hydrochloride). Subsequently, the polymer was placed in a flask and dissolved in methanol. The flask was placed in an ice bath and sodium methoxide solution (1.0 equiv., 25 wt % in methanol) was slowly added. The reaction was stirred for 1 h and sodium chloride was filtered off. The methanol was removed under reduced pressure and the neutralized polymer was dissolved in ethanol and purified by dialysis in distilled water using a 3500 g mol^{-1} cutoff membrane (Snakeskin, Pierce). After the residual ethanol was removed on the rotary evaporator, the polymer was obtained by freeze-drying as a white solid. Yield: 10.27 g (91%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.82−2.52 (2H, CH_2), 2.19−2.15 (3H, CH_3), 2.04−1.99 (2H, CH_2), 1.82−1.50 (2H, CH), 1.22−0.90 (4 h, CH_2).

2.6.2. Preparation of 1-Methylpyrrolidinium-Based Poly(ionic liquid)s. To poly(diallyl methyl amine) (1 equiv. with respect to monomer unit) DMF was added. The polymer did not dissolve until the alkyl iodides (1.2 equiv.) were slowly added and the quaternization reaction took place. The reaction was placed in an oil bath at 70 °C and after ca. 15 min the polymers were completely dissolved to give clear, slightly yellow solutions. To ensure completion of the quarternization the reaction was held at 60 °C for 48 h. The reaction was allowed to cool to room temperature and most of the DMF was removed under reduced pressure to obtain concentrated solutions of the formed poly(ionic liquid)s. The viscous liquids were washed with cold diethylether (3x) and the polymers were dried under reduced pressure. To aqueous poly(ionic liquid) solutions (1.0 equiv. with respect to monomer unit) bis(trifluoromethane)sulfonimide (LiTFSI, 1.2 equiv.) aqueous solution was slowly added and the reaction mixtures were stirred at room temperature. The poly(ionic liquid)s precipitated from the medium due to an anion exchange of the iodide

by the hydrophobic TFSI anion. The obtained poly(ionic liquid)s were successively washed with water several times. The aqueous phases were tested with AgNO$_3$ until all lithium iodide was removed. Residual water was removed by freeze-drying.

2.6.2.1. Poly[1-butyl-1-methylpyrrolidinium] Bis-(trifluoromethane)sulfonimide (PIL1). The general procedure was followed starting from poly(diallyl methyl amine) (13.5 mmol, 1.5 g) and 1-bromobutane (16 mmol, 2.22 g) in DMF (10 mL) to obtain the bromide poly(ionic liquid). For the anion exchange, bis-(trifluoromethane)sulfonimide lithium salt (17 mmol, 4.96 g) aqueous solution was slowly added to poly[1-butyl-1-methylpyrrolidinium] iodide aqueous solution. The polymer was obtained as a white solid. Yield: 5.55 g (91%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 4.00 (2H, CH_2), 3.44−3.17 (6H, CH_2), 2.75 (2H, CH), 1.81 (2H, CH_2), 1.66−1.45 (4H, CH_2), 1.38 (3H, CH_3), 0.96 (3H, CH_3).

2.6.2.2. Poly[1-(2-methoxyethyl)-1-methylpyrrolidinium] Bis-(trifluoromethane)sulfonimide (PIL2). The general procedure was followed starting from poly(diallyl methyl amine) (13.9 mmol, 1.55 g) and (2-methoxyethoxy)ethyl iodide (17 mmol, 3.16 g) in DMF (10 mL) to obtain the iodide poly(ionic liquid). For the anion exchange bis(trifluoromethane)sulfonimide lithium salt (19 mmol, 5.36 g) aqueous solution was slowly added to poly[1-(2-methoxyethyl)-1-methylpyrrolidinium] iodide aqueous solution. The polymer was obtained as a soft yellowish solid. Yield: 5.74 g (91%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 4.13 (2H, CH_2), 3.88 (2H, CH_2), 3.73−3.68 (2H, CH_2), 3.38−3.24 (7H, CH_2, CH_3), 2.76 (2H, CH), 1.67−1.46 (4H, CH_2).

2.6.2.3. Poly[1-(2-(2-methoxyethoxy)ethyl)-1-methylpyrrolidinium] Bis(trifluoromethane)sulfonimide (PIL3). The general procedure was followed starting from poly(diallyl methyl amine) (11.7 mmol, 1.30 g) and 2-(2-methoxyethoxy)ethyl iodide (14 mmol, 3.22 g) in DMF (10 mL) to obtain the iodide poly(ionic liquid). For the anion exchange bis(trifluoromethane)sulfonimide lithium salt (15 mmol, 4.38 g) aqueous solution was slowly added to poly[1-(2-(2-methoxyethoxy)ethyl)-1-methylpyrrolidinium] iodide aqueous solution. The polymer was obtained as a soft yellowish solid. Yield: 5.35 g (92%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 4.15 (2H, CH_2), 3.98 (2H, CH_2), 3.66−3.54 (6H, CH_2), 3.32−3.24 (7H, CH_2, CH_3), 2.76 (2H, CH), 1.65−1.45 (4H, CH_2).

2.6.2.4. Poly[1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1-methyl-pyrrolidinium] Bis(trifluoromethane)sulfonimide (PIL4). The general procedure was followed starting from poly(diallyl methyl amine) (10.3 mmol, 1.15 g) and 2-(2-(2-methoxyethoxy)ethoxy)ethyl iodide (13 mmol, 3.56 g) in DMF (10 mL) to obtain the iodide poly(ionic liquid). For the anion exchange bis(trifluoromethane)sulfonimide lithium salt (14 mmol, 4.09 g) aqueous solution was slowly added to poly[1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1-methylpyrrolidi-nium] iodide aqueous solution. The polymer was obtained as a soft yellowish solid. Yield: 5.05 g (91%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 4.19 (2H, CH_2), 4.02 (2H, CH_2), 3.73−3.51 (10H, CH_2), 3.35−3.27 (7H, CH_2, CH_3), 2.78 (2H, CH), 1.69−1.47 (4H, CH_2).

2.7. Preparation of the Electrolyte Blends. For the preparation of the binary electrolyte mixtures, PIL1, PIL2, PIL3, and PIL4, respectively, were mixed with IL2 in different weight ratios (20/80, 40/60, 60/40, 80/20) under magnetic stirring for 2 h. In addition, a ternary mixture of PIL4, IL2 and LiTFSI with a weight ratio of 40/50/10 was prepared. To favor the solubility of the PILs in the IL, we heated the mixtures to 50 °C. The blends were dried at 120 °C for 24 h before the conductivity measurements.

2.8. Characterization. Infrared spectra were recorded with an Avatar 360 FT-IR Thermo Nicolet spectrometer. The NMR spectra were recorded with a Bruker Avance III NMR spectrometer in appropriate deuterated solvents. Thermogravimetric analyses (TGA) were performed using a Q500 TG-DTA analyzer manufactured by TA Instruments in the temperature range between 25 and 600 °C, under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Thermal analyses were performed on a DSC instrument from Perkin-Elmer (Pyris Diamond DSC) over a temperature range from −80 to 180 °C under nitrogen. The glass transition temperature (T_g) was obtained as

the inflection point of the heat flow step, recorded at a scan rate of 20 °C/min. The melting points and the enthalpies for indium (mp 156.6 °C, AHm 28.5 J/g) and n-dodecane (mp 9.65 °C, AHm 218.73 J/g) were used for the temperature and the heat capacity calibration. Specific conductivity measurements were carried out in an electrochemical cell using platinum electrodes (the cell constant was determined with 0.1 M KCl) by impedance spectroscopy measurements on a Eco Chemie Autolab PGSTAT30 Potentiostat/Galvanostat in the frequency range 0.01 to 1×10^6 Hz.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Materials. The synthesis of iodine-terminated PEG chains was carried out using a direct and fast approach. In the first step, tosylation of the primary alcohols was carried out.[18] In a second step, the p-toluenesulfonate derivatives were dissolved in acetone, then sodium iodide was added and the reaction mixture was stirred at room temperature under nitrogen in the dark.[19] Scheme 1 displays the reaction scheme of the PEG functional groups.

Scheme 1. Synthesis of Alkyl Iodides
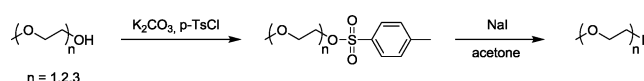
The ionic liquids and poly(ionic liquid)s were obtained by quaternization of methylpyrrolidine. The synthesis of the ionic liquids was carried out by adapting literature procedures.[5,20] For the obtainment of the poly(ionic liquid)s, first, diallyl methyl amine hydrochloride monomer was synthesized using a modified Eschweiler−Clark reaction (Scheme 2a).[16,17]

Scheme 2. Synthesis of (a) Diallyl Methyl Amine Hydrochloride Monomer and (b) Poly(diallyl methyl amine)
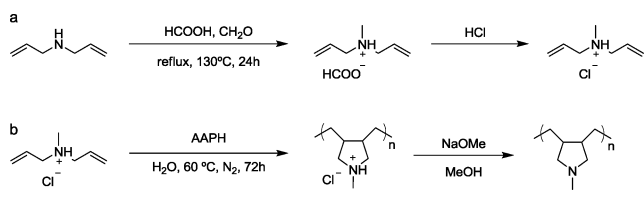
This reaction allowed for the obtainment of large amounts of the monomer from inexpensive starting materials. The versatile monomer can be neutralized with sodium methoxide or sodium hydroxide either in methanol or water and subsequently quaternized with halogen-terminated groups. The subsequent polymerization of these functionalized monomers can yield a wide range of novel pyrrolidinium-based poly(ionic liquid)s. Our initial experiments showed that diallyl methyl amine polymerized even when functionalized with groups such as butyl, amine, alcohol, or carboxyl. In this work, we modified neutralized diallyl methyl amine with PEG groups. Unfortunately, we found that these monomers did not polymerize although several different reaction conditions were applied (see Supporting Information). This behavior may be related to the nature of the PEG groups and/or inherent difficulties related to allyl polymerization.[21] Therefore, diallyl methyl amine hydrochloride was first polymerized in water by free-radical polymerization using 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AAPH) initiator, neutralized (Scheme 2b) and subsequently functionalized with different PEG groups. A PIL with butyl group was synthesized as a reference. The iodide

counteranion was replaced by the fluorinated $[NTf_2]^-$ (or TFSI) anion using a simple anion exchange. Size-exclusion chromatography analyses did not yield any useful data for the determination of the molecular weights of the PILs. Therefore, MALDI-TOF was used as an alternative characterization method. A molecular weight of ca. 40 000 g/mol was obtained for the precursor poly(diallyl methyl amine) (see the Supporting Information). The highly charged PILs (PIL1-PIL4) could not be detected by this technique, though it is assumed that the chain length of the polymer backbone remained unaltered during the quaternization step. The synthesis scheme of the ILs and PILs is shown in Scheme 3.

Scheme 3. Synthesis of (a) ILs and (b) PILs with Pendant PEG Chains
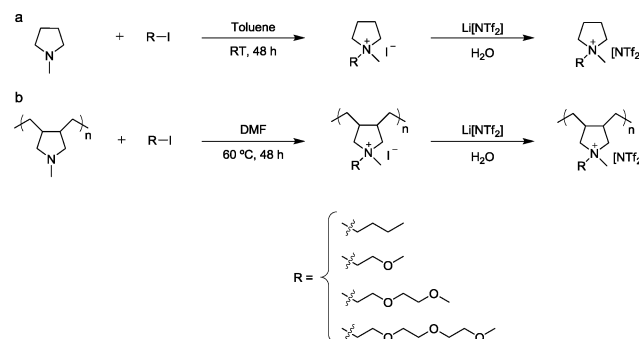
3.2. Nuclear Magnetic Resonance Spectroscopy (NMR). NMR spectroscopy was used to investigate the chemical structure of the polymers PIL1, PIL2, PIL3, and PIL4. In Figure 1, the ^1H NMR spectra of the new pyrrolidinium poly(ionic liquid)s are displayed.

The values obtained from the integration of the peaks let us assume that the yields of the quaternization reactions lay between 70 and 90%. In all spectra a splitting of the peaks belonging to the polymer backbone and the five-membered pyrrolidinium ring was observed, which can be related to the presence of cis and trans isomers. ^{13}C NMR confirmed the presence of stereoisomers (see the Supporting Information). Earlier studies also reported on splitting for free radical and RAFT polymerized poly(diallyldimethyl)ammonium-based polymers.[22,23]

3.3. Thermogravimetric Analysis (TGA). The thermal stability of the designed ILs and PILs was studied by TGA. Previous studies have shown that the anion $[NTf_2]^-$ attributes excellent thermal properties to ILs and PILs in comparison to other fluorinated or halogenated anions.[24] To illustrate this fact, the TGA curves of the obtained ILs and PILs are shown in Figure 2. All ILs and PILs exhibit a high thermal stability with thermal degradation temperatures above 300 °C.

It can be seen that the thermal stability of the PILs is slightly lower compared to the one of their IL homologues. Similar observations were made previously where PILs and their corresponding monomeric ILs showed comparable thermal stabilities.[25,26] For both, the ILs and the PILs it was observed that the best performance was obtained with the butyl side chain (IL1 = PYR$_{14}$TFSI, PIL1). However, the PILs and ILs with PEG side chains showed only slightly lower degradation temperatures. In Figure 2 the temperatures corresponding to a 5% mass loss, T_d, and at which the degradation is maximal, $T_{d,max}$ are listed. It can be observed that the thermal stability decreases somewhat with an increase in the PEG side chain

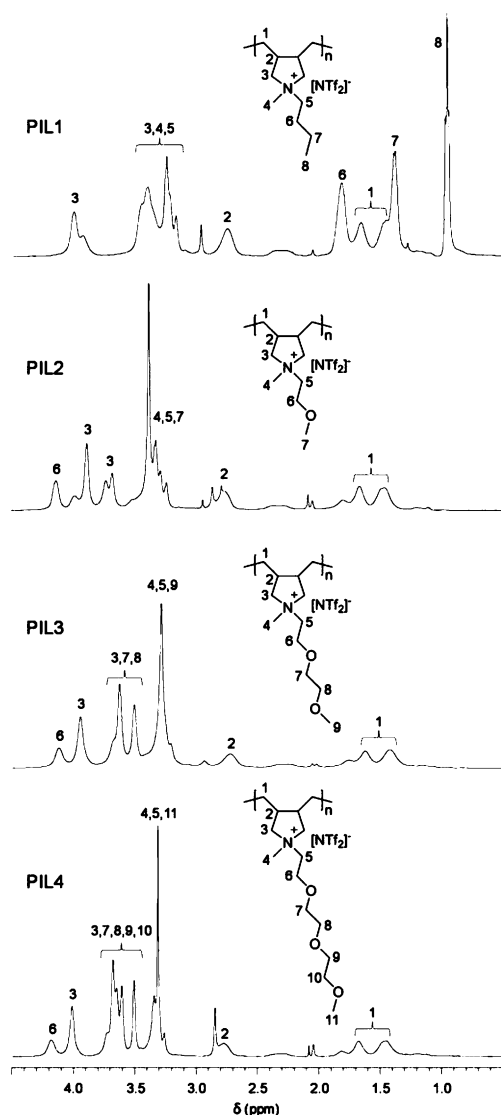**Figure 1.** ^{1}H spectra of PILs with pendant PEG chains.

Figure 2. TGA of (a) ILs and (b) PILs with PEG side chains.
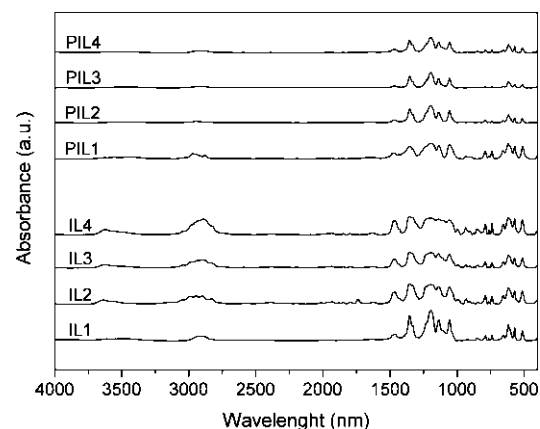
Figure 3. FTIR of ILs and PILs with PEG side chains.

length, contrary to previous studies with aromatic imidazolium-based ionic liquids, where T_d slightly increased with an increase in the PEG side-chain length. The latter was explained by a wrapping of the PEG tails (7−16 ethylene glycol units) around the aromatic imidazolium ring.[3,27] The slight decrease in the degradation temperature of the here presented ILs and PILs could be related to the shorter PEG groups (1−3 ethylene glycol units). Though, all synthesized materials possess a very good thermal stability, which makes them suitable for a wide range of electrochemical applications.

3.4. Infrared Spectroscopy (FTIR). Infrared spectroscopy (FTIR) of all compounds was conducted for the evidence of the presence of the $[NTf_2]^-$ counteranion after the anion exchange reactions. The spectra of the ILs and PILs are summarized in Figure 3. In all the spectra the characteristic bands corresponding to the $[NTf_2]^-$ anion can be observed at around 1348, 1196, 1136, and 1055 cm^{-1}.[11] FTIR spectroscopy thus confirms the correct formation of all ILs and PILs.

3.5. Ionic Conductivity. In Figure 4, the ionic conductivity of the synthesized ILs with pendant PEG chains (IL2, IL3, and IL4) is compared to the conductivity of commercial PYR$_{14}$TFSI (IL1) with butyl group. It can be observed that the conductivity

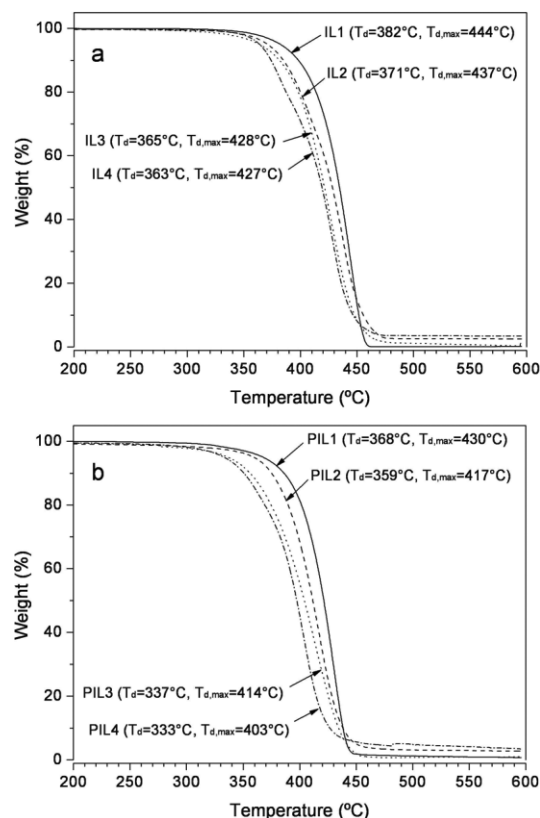of all ILs agrees well with the Arrhenius equation in the measured temperature range (25−100 °C) following the trend IL1 ≈ IL4 < IL3 < IL2. In the case of the ILs with PEG groups, the conductivity decreases with an increase in the PEG chain length. This trend can be explained through an increase in the viscosity, a behavior that has been reported previously for PEG functionalized ILs.[3] It can further be seen that all PEG-ILs have a higher conductivity than the commercial PYR$_{14}$TFSI (IL1) except IL4, the IL with the longest PEG chain, which has a very similar conductivity. This behavior can be attributed to the effect of oxygen atoms in the lateral PEG side chains which lower the viscosity compared to common alkylpyrrolidinium-based ILs.[5,20] As a comparison, at 25 °C PYR$_{14}$TFSI (IL1) has a conductivity of 2.2 mS cm^{-1}, whereas IL2 nearly doubles this value with 3.9 mS cm^{-1}. The measured conductivity values are

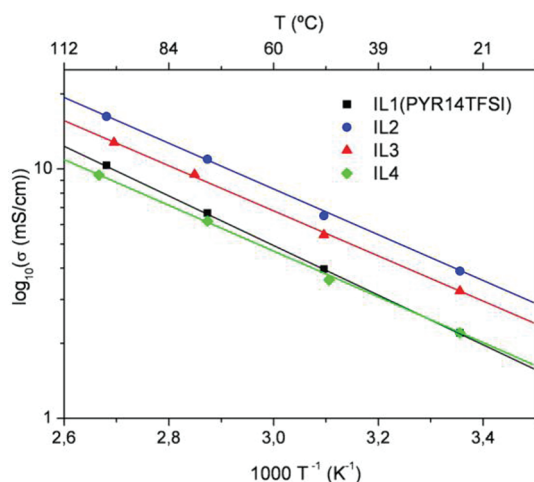**Figure 4.** Ionic conductivity of ILs with PEG side chains and commercial PYR$_{14}$TFSI.

in good accordance with previously reported measurements of pyrrolidinium ILs with PEG side chains which showed conductivities of 1−7 mS cm^{-1} in a temperature between 20 and 60 °C.[5]

Next, blends of IL2, the IL of the series with the highest conductivity, and the PILs (PIL1 with butyl side chain as a reference and PIL2, PIL3, and PIL4 with PEG groups) were prepared. For the electrolyte blends, PIL/IL mixtures with a weight ratio of 20/80 were prepared. Figure 5 plots the results of the conductivity measurements.
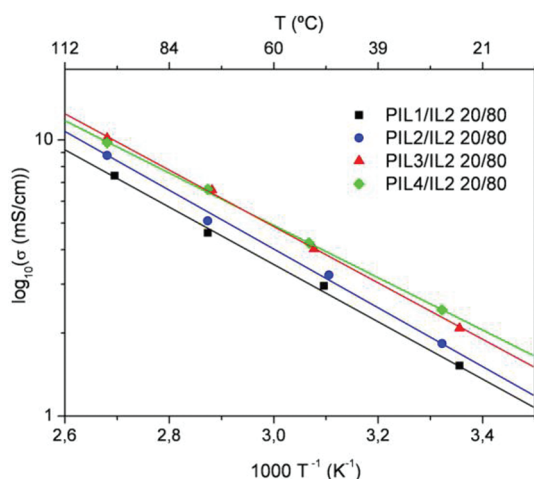

Figure 5. Ionic conductivity of PIL/IL blends with a weight ratio of 20/80.

It can be observed that the blends PIL4/IL2 and PIL3/IL2, i.e. the PILs with the longest PEG side chains, provide the best performances with a conductivity of 2.1−2.4 mS cm^{-1} at 25 °C and 9.8−10.2 mS cm^{-1} at 100 °C. The overall trend, which follows PIL1/IL2 < PIL2/IL2 < PIL3/IL2 ≈ PIL4/IL2, illustrates that the conductivity of the blends increases with an increase in the PEG side-chain length. For the reference blend PIL1/IL2, i.e. the butyl-substituted PIL, the lowest conductivity was measured.

To determine the best performing PIL of the series, we prepared mixtures with different PIL/IL weight ratios of PIL3 and PIL4, respectively, and IL2. Figure 6 compares the
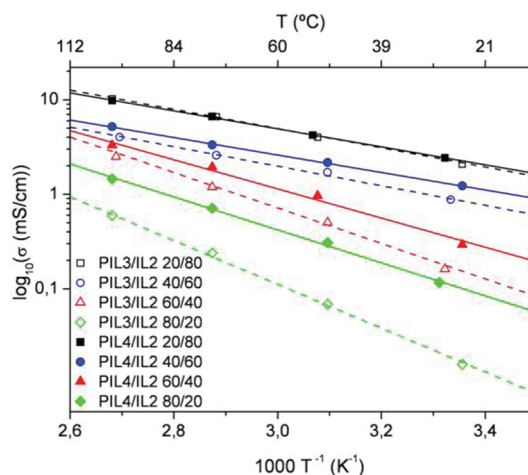

Figure 6. Ionic conductivity of PIL/IL blends with different weight ratios.

conductivity of PIL3/IL2 and PIL4/IL2 electrolyte blends with weight ratios of 20/80, 40/60, 60/40, and 80/20.

Although both electrolyte systems show a similar conductivity for the 20/80 PIL/IL blend, the conductivity of the PIL4/IL2 blends is always higher than the conductivity of the PIL3/IL2 blends when the PIL/IL ratio is increased in favor of the PIL. Obviously, the conductivity decreases when the PIL/IL ratio is increased in favor of the PILs, because of an increase in the viscosity of the systems. It is worth remarking that all blends dissolve fully in acetone, and therefore polymeric electrolyte membranes can be obtained by doctor-blade techniques. Further attempts to produce PILs with even longer alkyl chains resulted in sticky polymeric materials with a very poor processability.

Electrolytes containing PILs for electrochemical applications such as lithium-ion batteries are usually obtained by preparing ternary mixtures of a poly(ionic liquid), an ionic liquid and a lithium salt to add electroactive Li$^+$ cations to the electrolyte for the battery reaction.[4] The standard salt that is used in this type of electrolytes is bis(trifluoromethane)sulfonimide lithium salt (LiTFSI). Hence, an electrolyte of the best performing PIL and IL and LiTFSI salt was prepared.

In Figure 7, the ionic conductivity of a PIL4/IL2/LiTFSI blend with a weight ratio of 40/50/10 is compared to pure IL2 and a blend of PIL4/IL2 with a weight ratio of 40/60.

As expected, for IL2, the highest conductivity with 3.9 mS cm^{-1} at 25 °C and 16.3 mS cm^{-1} at 100 °C was measured. Yet, for the 40/60 PIL4/IL2 blend, a very good conductivity of 1.2 mS cm^{-1} at 25 °C and 5.2 mS cm^{-1} at 100 °C was obtained. These results are better than those reported for binary blends with similar weight ratios obtained from commercial PYR$_{14}$TFSI and poly(diallyldimethylammonium) TFSI without PEG moieties (∼0.12 mS cm^{-1} at 25 °C and 1.5 mS cm^{-1} at 57 °C).[28] Also, the ternary 40/50/10 PIL4/IL2/LiTFSI blend performs better (0.44 mS cm^{-1} at 25 °C and 3.3 mS cm^{-1} at 100 °C) than ternary blends with similar weight ratios based on poly(diallyldimethylammonium) TFSI, PYR$_{14}$TFSI and LiTFSI (0.16 mS cm^{-1} at 20 °C) and is similar to ternary systems prepared with PEO, PYR$_{14}$TFSI and LiTFSI (0.37 mS cm^{-1} at 20 °C).[30] The electrochemical window of such PIL and PEO-based ternary electrolytes was reported to be wider than 5 V.[29] It is worth mentioning that these materials may also have potential applications in electrochemical devices such as solar
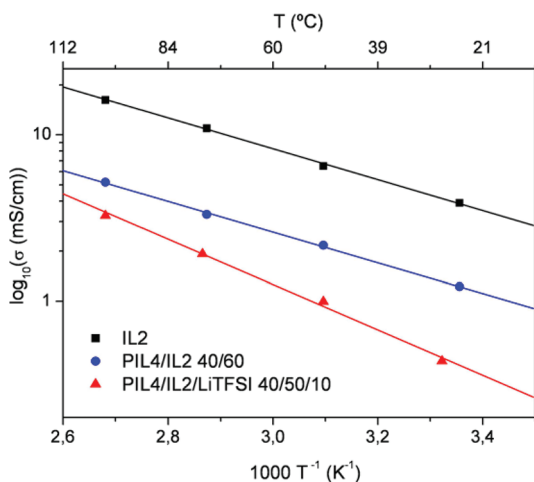
Figure 7. Ionic conductivity of different IL- and PIL-based electrolytes.

cells, as the initial PILs and ILs were obtained with iodide anion. Iodide ionic liquids have already successfully been applied as solvent-free electrolytes in dye sensitized solar cells.[30,31]

3.6. Thermal Analysis (DSC). Different to their IL counterparts, the ionic conductivity increased for PILs with longer PEG side chains. Thermal analysis (DSC) was used to study this behavior more in detail. Figure 8 shows the results obtained from DSC measurements.
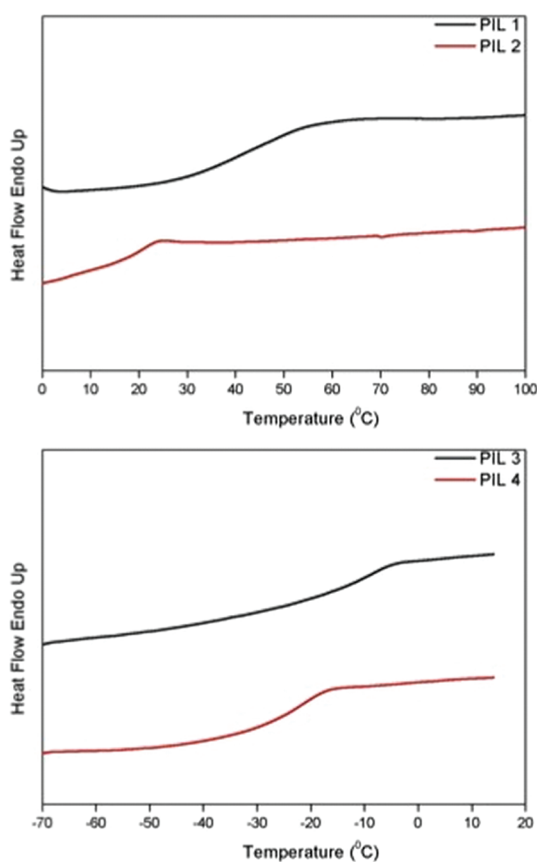

Figure 8. Differential scanning calorimetry (DSC) of PILs with pendant PEG chains.

Whereas PIL1 with a butyl group was a solid, rather hard polymer, PIL2 was already softer but still solid. PIL3 and PIL4 were very soft solids with PIL4 being the softest polymer of the series. Taking into account that all polymers were obtained from the same polymer precursor, i.e. same molecular weight, the softening and the enhancement in the conductivity can be attributed to the presence of the PEG moieties. For PIL 4, the polymers with the longest PEG chain (three ethylene oxide units) a T_g of -23.5 °C was obtained. PIL3 with a shorter PEG chain showed a T_g of -12.6 °C and PIL2 with the shortest PEG chain showed a T_g of 18.2 °C. For PIL1 with butyl side chain the highest T_g of 40.3 °C was determined. The results of the thermal analysis support the trend obtained from the conductivity measurements where the PILs with long PEG chains and a low T_g show the best performances. Accordingly, it has been reported that a decrease in T_g of poly(ionic liquid) materials results in an increase in their ionic conductivity. It is expected that the increased conductivity is the result of an increase in the free volume and a better polymer chain flexibility which facilitates the ion transport in the poly(ionic liquid)s.[2,32]

3. CONCLUSION

A new family of pyrrolidinium-based poly(ionic liquid) electrolytes with poly(ethylene glycol) side chains has been synthesized and characterized. Binary electrolyte mixtures were prepared by blending the poly(ionic liquid)s with chemically similar ionic liquids in different weight ratios. Furthermore, a ternary mixture based on the best performing poly(ionic liquid)/ionic liquid and bis(trifluoromethane)sulfonimide lithium salt was prepared. Specific conductivity measurements revealed that the ionic conductivity of the blends increased with an increase in the PEG chain length of the PILs, which can be attributed to an increase in the free volume and a better polymer chain flexibility which facilitates the ion transport in the poly(ionic liquid)s. It was also found that the electrolytes having PEG side chains performed better than their pyrrolidinium counterparts with a butyl side chain, which were synthesized as a reference. Currently, ternary polymer blends based on the described materials are being tested in lithium-ion batteries.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Reaction conditions for the polymerization, MALDI-TOF analysis, ^{13}C NMR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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