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Polymeric Ionic Liquids: Comparison of Polycations and Polyanions

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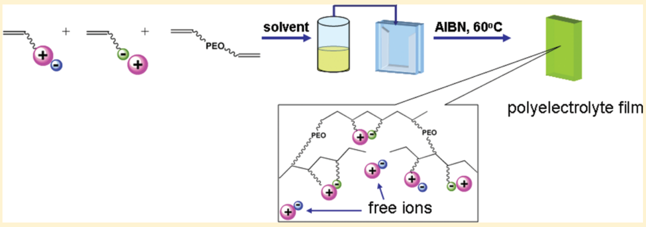
Supporting Information



ABSTRACT: The achievement of high ionic conductivity in new "polymeric ionic liquids" (PILs) is of great interest as it refers to the solid state electrolytes and their applications in electrochemistry. Four ionic monomers, including two new ones, namely *N*-[(2-methacryloyloxy)-propyl]-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (**M1**), 1-[2-(methacryloyloxy)propyl]-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (**M2**), *N*-methyl-*N*-ethylpyrrolidinium(3-sulfopropyl) methacrylate (**M3**), and 1-methyl-3-ethylimidazolium(3-sulfopropyl) methacrylate (**M4**), were prepared and used both for the synthesis of linear PILs and ionic networks with poly(ethylene glycol) dimethacrylate (**PEGDM**). The optimal polymerization conditions for obtaining high molar mass PILs (M_{sD} up to 1.24×10^6 g/mol) were identified. The copolymerization of oppositely charged monomers was studied as well. Polycations, polyanions, and their random ionic copolymers were compared in terms of their physical properties. The examined properties were found to depend mainly on the nature of the counterion. It became obvious that the bulk ionic conductivity of hydrophilic polyanions is greatly affected by the humidity. It increases up to 220 times upon transferring from dry air to 20% relative humidity. Ionic conductivity increased in random ionic copolymers synthesized from oppositely charged monomers feasibly, suggesting that the ion transport was improved by the partial formation of mobile ionic liquid within the polymer.

INTRODUCTION

Since the first observations on synthesis and bulk ionic conductivity of "polymeric ionic liquids" (PILs) made by Ohno and co-workers,[1] this class of solid polymer electrolytes has aroused strong interest.[2−4] PILs can be described as "*polymers which contain at least one ionic center, similar by composition to the structure of commonly used ionic liquids (ILs), as a covalently bonded part of their constitutional repeating (monomer) unit*".[3] Thus, PILs constitute a new class of polymer materials with exceptional and unique properties inherent for molten salts themselves.[5] In addition, PILs include a wide variety of structures and have the potential to show some specific functions such as transport of target ions, polar environment, and mechanical strength.[4,6]

PILs are predicted to be a promising material for the separation membranes in lithium batteries.[6] However, for such utilization a polymer electrolyte is required to possess high enough ionic conductivity and good mechanical stability. The challenge of current research in this field is to merge high ion conductivity with sufficient mechanical properties by the design of the corresponding ionic liquid-like monomers (ILMs).[3,4] The structural variations should follow some basic rules: the main polymer chain needs to be flexible,[3,7] the ionic center is preferred to be placed on the end of the polymer side chains,[8,9] and the complex structure of the spacer is expected to be partly comprised of oxygen atoms.[10] All these concepts are believed to provide a large segmental mobility, which is necessary for good

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ion motion. According to the recent reports,[4,11−13] the designed PIL should refer to the polyanion type.

Apart from the structural variations of the ionic monomers, the bulk conductivity of polyelectrolyte films can be successfully increased by the copolymerization of the ILMs with nonionic monomers. Such approach helps to decrease the ion−ion interaction in PIL by the introduction of the neutral side chains and simultaneously to increase the flexibility of the polyelectrolyte chain or to reduce the copolymer's glass transition temperature (T_g). This solution was successfully applied by Elabd[14] and Dutta.[15] When 1-[2-methacryloyloxy)ethyl]-3-butylimidazolium tetrafluoroborate was copolymerized with hexyl methacrylate (HMA), the bulk ionic conductivity of the nonionic−ionic copolymer was increased by more than 1 order of magnitude.[14] Even though the overall charge carrier number was reduced with the rise of the HMA content, the copolymer conductivity was increased due to the significant lowering of T_g. In a similar manner the copolymerization of *N*-vinylpyridine with HMA resulted in the improvement of polymer flexibility and as a consequence in the decrease of the T_g of the copolymers.[15] It should be mentioned that such improvement of ionic conductivity is passing through a maximum; i.e. initially, the gradual increase in the nonionic monomer content results in the decrease of the T_g of the copolymers and in the rise of the conductivity due to the increased ion mobility. However, after reaching a certain content of nonionic monomer, the conductivity starts to decrease owing to the reduction of the density of the free ions.

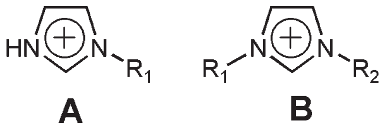
As an alternative approach, polyelectrolyte multilayers (PEM) are promising, since their multiple electrostatic interactions provides quite good mechanical stability for the material, while at the same time ultrathin membranes of nanometric dimensions can be fabricated.[16] PEMs can be produced by layer-by-layer assembly, i.e., the alternating adsorption of polycations and polyanions. Nevertheless, strong hydration is needed very often for PEM films to achieve good dissociation and sufficient ionic conductivity due to the limited mobility of the charge carriers.[17,18]

Another interesting method to increase the bulk ionic conductivity is the copolymerization of oppositely charged ionic monomers. This pathway was realized by Ohno et al. with the goal to improve the migration of lithium cations and to enlarge the lithium ion transference number (t_{Li^+}).[19,20] In such a way, methacryloyl octa(ethylene oxide)-2-sulfobenzoate lithium salt (PE8 monomer) was copolymerized with the more conductive 1-[6-(acryloyloxy)hexyl]-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide (C_6EIm monomer).[19] It was found that the conductivity improved by increasing the number of C_6EIm monomer units. In contrast, higher t_{Li^+} values were observed with increase of the PE8 units content. In general, the ionic conductivity of the obtained copolymers was intermediate in comparison with the conductivity values of the respective homopolymers. This was explained by a poor dissociation state of the copolymers.[19]

To our knowledge, by now, the investigated PILs of polyanion type were merely prepared from the monomers containing protonated or protic imidazolium cations as mobile counterions (Scheme 1, structure A).[3] Until recently, the only work dedicated to PIL with noncovalent bonded quaternized or aprotic imidazolium cation (Scheme 1, structure B) was reported.[12]

Accordingly, the present work is devoted, first, to the design and synthesis of novel ILMs with quaternized cations, second, to the determination of the optimal polymerization conditions, third, to the study of the physical properties of the polyelectrolytes and to the comparison of structurally similar PILs of the polyanion and polycation type, and, finally, to the copolymerization of oppositely charged ILMs with the goal to achieve in the polyelectrolyte both noncovalently bonded cations and anions that can dissociate and associate, thus forming highly conductive IL within the polymer matrix.

Scheme 1. Chemical Structure of Protic (A) and Quaternized (Aprotic) (B) Imidazolium Cations



EXPERIMENTAL SECTION

Materials. Poly(ethylene glycol) dimethacrylate (**PEGDM**, M_w = 750 g/mol, Aldrich), 4-methoxyphenol (99%, Acros), lithium bis(trifluoromethylsulfonyl)amide (≥99%, Aldrich), ionic exchange resin Amberlite Ira-400(Cl) (Aldrich), phosphorus pentoxide (98%, Alfa Aesar), ethanol (HPLC grade, Carlo Erba), methanol (Carlo Erba), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, ≥99%, Aldrich), and dicyclohexylperoxydicarbonate (DCPD, initiator, Groupe Arnaud) were used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN, initiator, 98%, Acros) was recrystallized from methanol before use. 1-Bromoethane (98%, Acros), 3-bromopropanol-1 (97%, Aldrich), *N*-methylpyrrolidine (98%, Acros), and *N*-methylimidazole (99%, Acros) were distilled under inert gas over CaH_2. Reagent-grade chloroform, acetonitrile, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), dimethyl sulfoxide (DMSO), dichloromethane, ethyl acetate, and diethyl ether were obtained from Aldrich, Acros, or Merck and were purified by vacuum distillation over P_2O_5. Methacryloyl chloride (97%, Fluka) was distilled prior to use. 3-Sulfopropyl methacrylate potassium salt (SPMA, 98%, Aldrich) was carefully dried under vacuum (<1 mmHg) at 25 °C for 2 h prior to use.

Ionic Liquids. 1-Methyl-3-ethylimidazolium bromide and *N*-methyl-*N*-ethylpyrrolidinium bromide were synthesized as published previously.[21] 1-Methyl-3-ethylimidazolium chloride and *N*-methyl-*N*-ethylpyrrolidinium chloride were obtained by passing a 5 wt % bromide salt aqueous solution through the column filled with Cl-loaded ion-exchange resin (Amberlite Ira-400(Cl)). After the evaporation of water, the white solid was thoroughly dried for 48 h at 60 °C /<1 mmHg with a special flask/trap filled with P_2O_5 and introduced into the vacuum line. The synthesized ILs were characterized by elemental and Karl Fisher analysis, NMR, and IR spectroscopy. The purity of ILs was higher than 98%.

***N*-[(2-Methacryloyloxy)propyl]-*N*-methylpyrrolidinium Bis(trifluoromethylsulfonyl)amide (M1).** **M1** was synthesized similarly to the procedure published previously.[22] Thus, *N*-(3-hydroxypropyl)-*N*-methylpyrrolidinium bromide and *N*-(3-hydroxypropyl)-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide were prepared in accordance with ref 22. The obtained compounds were characterized by elemental analysis, NMR, and IR spectroscopy. However, the third stage was modified as follows:

The methacryloyl chloride (4.82 g, 0.046 mol) was placed in a round-bottom flask and was cooled in an ice bath under inert gas to 0−1 °C. The freshly prepared *N*-(3-hydroxypropyl)-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (13.05 g, 0.031 mol) was slowly added dropwise to the cooled methacryloyl chloride with gentle stirring. The stirring was continued at 0−1 °C for 1.5 h, then at room temperature for 5 h, and finally at 40 °C for 12 h. To remove the excess of methacryloyl chloride, the obtained oil was thoroughly washed with diethyl ether (5 × 15 mL). After evaporation of residual diethyl ether, the reaction mixture was redissolved in dichloromethane and the solution was washed with water (3 × 15 mL). The organic layer was then dried over $MgSO_4$, and the catalytic amount of 4-methoxyphenol as an inhibitor was added. The dichloromethane was evaporated at 25 °C under vacuum, and the product as slightly yellow transparent oil was dried at 25 °C/12 mm for 2 h and additionally at 25 °C/1−2 mm for 2 h. [Hereinafter, all liquid compounds were dried at specified temperature with a special flask filled with P_2O_5 and introduced into the vacuum line, whereas solid polymers and films were dried in the vacuum oven containing a Petri dish with phosphorus pentoxide.] Yield: 9.52 g (63%). Anal. Calcd for $C_{14}H_{22}F_6N_2O_6S_2$ (492.45): C, 34.15%; H, 4.50%; F, 23.15%. Found: C, 34.13%; H, 4.76%; F, 23.10%. ^{1}H NMR (400.13 MHz, $CDCl_3$): 5.97 (s, 1H, $\underline{CH_2}{=}C(CH_3){-}$), 5.48 (t, 1H, J_{HH} = 2.0 Hz, $\underline{CH_2}{=}C(CH_3){-}$), 4.08 (t, 2H, J_{HH} = 8.0 Hz, $CO{-}O{-}\underline{CH_2}{-}$), 3.47−3.30 (m, 6H, $-CH_2-\underline{CH_2}-CH_2-N$ and $-N(\underline{CH_2})_2$ (Pyrr)), 2.94 (s, 3H, $N\underline{CH_3}$), 2.13 (m, 4H, $CH_2-(\underline{CH_2})_2-CH_2$, (Pyrr)), 2.06 (t, 2H, J_{HH} = 8.0 Hz, $-CH_2-CH_2-\underline{CH_2}-N$), 1.79 (s, 3H,$CH_2{=}C(\underline{CH_3}){-}$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 166.7 (C=O), 135.2, 126.0, 125.8−112.8 (q, anion, J_{CF} = 428 Hz), 64.3, 61.4, 60.6, 47.8, 22.9, 21.0 ($-CH_2-N-\underline{CH_3}$ (Pyrr)), 17.7 ($CH_2{=}C(\underline{CH_3}){-}$). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −79.3 (s, CF_3). IR (KBr pellet): 3037 (w, ν_{C-H}), 2985 (m, ν_{C-H}), 2904 (w, ν_{C-H}), 1719 (s, $\nu_{C=O}$), 1638 (m, $\nu_{C=C}$), 1467 (m), 1457 (m), 1436 (w), 1405 (w), 1353 (vs, ν_{asSO_2}), 1332 (s), 1299 (m), 1227 (s), 1193 (vs, ν_{CF}), 1140 (s, ν_{sSO_2}), 1057 (vs, ν_{CF}), 945 (m), 909 (w), 816 (w), 790 (m), 763 (w), 740 (m), 654 (m), 618 (s), 601 (m), 571 (s), 515 (s) cm^{-1}. T_g = −69.1 °C.

1-[2-(Methacryloyloxy)propyl]-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide (M2). **M2** was prepared in accordance with the procedure described for **M1**. It was isolated as colorless viscous oil. Yield: 66%. Anal. Calcd for $C_{13}H_{17}F_6N_3O_6S_2$ (489.40): C, 31.90%; H, 3.50%; F, 23.29%. Found: C, 31.47%; H, 3.43%; F, 23.32%. ^{1}H NMR (400.13 MHz, acetone-d_6): 8.71 (s, 1H, H2 (Im)), 7.46 (s, 1H, H3 (Im)), 7.37 (s, 1H, H4 (Im)), 5.71 (s, 1H, $\underline{CH_2}{=}C(CH_3){-}$), 5.31 (s, 1H, $\underline{CH_2}{=}C(CH_3){-}$), 4.21−4.17 (m, 2H, $CO{-}O{-}\underline{CH_2}{-}$), 3.93−3.90 (m, 2H, $-O-CH-\underline{CH_2}-CH_2-N$), 3.71 (s, 3H, $CH_2{=}C(\underline{CH_3}){-}$), 1.76−1.72 (m, 2H, $-O-CH-CH_2-\underline{CH_2}-N$), 1.56 (s, 3H, $N\underline{CH_3}$). ^{13}C NMR (100.61 MHz, acetone-d_6): δ = 167.3 (C=O), 137.6, 137.0, 125.9, 125.7−116.1 (q, anion, J_{CF} = 321.2 Hz), 124.9, 123.5, 61.9, 47.8, 36.6 ($N-\underline{CH_3}$), 18.3 ($CH_2{=}C(\underline{CH_3}){-}$). ^{19}F NMR (376.50 MHz, acetone-d_6): δ = −79.9 (s, CF_3). IR (KBr pellet): 3158 (m, ν_{C-H}), 3123 (m, ν_{C-H}), 2966 (w, ν_{C-H}), 1718 (s, $\nu_{C=O}$), 1636 (w, $\nu_{C=C}$), 1576 (m), 1457 (m), 1352 (vs, ν_{asSO_2}), 1332 (vs), 1298 (m), 1229 (vs), 1193 (vs, ν_{CF}), 1140 (vs, ν_{sSO_2}), 1057 (vs, ν_{CF}), 949 (w), 790 (m), 763 (w), 741 (m), 653 (m), 617 (s), 571 (s), 514 (s), 435 (w) cm^{-1}. T_g = −68.3 °C.

***N*-Methyl-*N*-ethylpyrrolidinium(3-sulfopropyl) Methacrylate (M3).** To the solution of 5.79 g (0.039 mol) of *N*-methyl-*N*-ethylpyrrolidinium chloride and 0.009 g of 4-methoxyphenol (as inhibitor) in 10 mL of acetonitrile the solution of 9.56 g (0.039 mol) of 3-sulfopropyl methacrylate potassium salt in 20 mL of acetonitrile was added dropwise under inert gas. The reaction mixture was stirred at room temperature overnight. The precipitated potassium chloride was removed by filtration and washed with fresh acetonitrile. The acetonitrile solutions were combined, and the solvent was gently removed at temperature ≤30 °C to prevent unwanted polymerization. The residue was redissolved in dry DCM and was kept at −18 °C for 2 h, giving a slightly opalescent solution, which was filtered off and the solvent was removed under vacuum at ambient temperature. The product, a slightly yellow oil, was dried at $T < 30$ °C/<1 mmHg for 1 h. Yield: 12.1 g (97%). Anal. Calcd for $C_{14}H_{27}NO_5S$ (321.43): C, 52.31%; H, 8.47%; N, 4.36%; S, 9.97%. Found: C, 51.85%; H, 8.58%; N, 4.42%. ^{1}H NMR (400.15 MHz, D_2O): δ = 0.84 (t, 3H, J = 7.2 Hz, $\underline{CH_3}CH_2N$), 1.23−1.32 (m, 2H, $CH_2\underline{CH_2}CH_2SO_3$), 1.63−1.70 (m, 2H, $\underline{CH_2}SO_3$), 1.82 (s, 3H, $CH_2{=}C(\underline{CH_3}){-}$), 2.09 (s, 4H, $NCH_2\underline{CH_2}CH_2$), 2.92 (s, 3H, $\underline{CH_3}N$), 3.19−3.23 (q, 2H, J_{HH} = 7.2 Hz, $CH_3\underline{CH_2}N$), 3.38−3.39 (m, 4H, $N\underline{CH_2}CH_2CH_2$), 4.17 (t, 2H, J_{HH} = 6.2 Hz, $CH_2\underline{CH_2}OC(O)$), 5.61 (t, 1H, J_{HH} = 1.5 Hz, $\underline{CH_2}{=}C(CH_3){-}$), 6.04 (s, 1H, $\underline{CH_2}{=}C(CH_3){-}$). ^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 8.76, 17.89, 20.98, 24.79, 46.77, 47.76, 58.21, 62.76, 63.65, 125.38, 135.90, 166.43. IR (KBr pellet): 3104 (w), 3109 (w), 2978 (s), 2930 (m), 2896 (w), 1715 (vs, $\nu_{C=O}$), 1637 (m, $\nu_{-C=C-}$), 1571 (w, pyrrolidinium ring), 1473 (m), 1455 (m), 1321 (s), 1298 (s), 1195 (vs, RSO_3, ν_{asSO_2}), 1059 (m), 1037 (vs, RSO_3, ν_{sSO_2}), 1018 (m), 1000 (w), 941 (m, δ_{CH}), 817 (m), 786 (w), 728 (m), 651 (w), 613 (m, RSO_3, ν_{S-O}), 598 (w), 523 (m) cm^{-1}. T_g = −80.5 °C.

1-Methyl-3-ethylimidazolium(3-sulfopropyl) Methacrylate (M4). **M4** was prepared from 3-sulfopropyl methacrylate potassium salt and 1-methyl-3-ethylimidazolium chloride according to the procedure described for **M3** and was isolated as slightly yellow oil. Yield: 98%. Anal. Calcd for $C_{13}H_{22}N_2O_5S$ (318.39): C, 49.04%; H, 6.96%; N, 8.80%; S, 10.07%. Found: C, 48.77%; H, 7.04%; N, 8.81%. ^{1}H NMR (300.15 MHz, D_2O): δ = 1.41 (t, 3H, J_{HH} = 7.2 Hz, $\underline{CH_3}CH_2N$), 1.87 (s, 3H, $CH_2{=}C(\underline{CH_3}){-}$), 2.03−2.13 (m, 2H, $CH_2\underline{CH_2}CH_2SO_3$), 2.97 (m, 2H, $\underline{CH_2}SO_3$), 3.82 (s, 3H, $\underline{CH_3}N$), 4.12−4.19 (q, 2H, J_{HH} = 7.2 Hz, $CH_3\underline{CH_2}N$), 4.22 (t, 2H, J_{HH} = 6.3 Hz, $CH_2\underline{CH_2}OC(O)$), 5.65 (t, 1H, J_{HH} = 1.5 Hz, $\underline{CH_2}{=}C(CH_3){-}$), 6.08 (s, 1H, $\underline{CH_2}{=}C(CH_3){-}$), 7.35 (t, 1H, J_{HH} = 1.5 Hz, H5 (Im)), 7.42 (t, 1H, J_{HH} = 1.5 Hz, H5 (Im)), 8.64 (s, 1H, H2 (Im)). ^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 15.03, 17.88, 24.77, 35.56, 44.00, 47.78, 63.63, 121.88, 123.47, 125.38, 135.89, 136.27, 166.42. IR (KBr pellet): 3146 (w), 3095 (m), 2978 (m), 2929 (w), 1715 (vs, $\nu_{C=O}$), 1637 (m, $\nu_{-C=C-}$), 1574 (s, imidazolium ring), 1453 (m), 1322 (s), 1298 (s), 1195 (vs, RSO_3, ν_{asSO_2}), 1176 (vs), 1059 (m), 1037 (vs, RSO_3, ν_{sSO_2}), 1019 (m), 944 (w, δ_{CH}), 855 (w), 817 (w), 786 (m), 728 (m), 651 (w), 612 (m, RSO_3, ν_{S-O}), 598 (w), 524 (m) cm^{-1}. T_g = −79.1 °C.

Typical Procedure for the Free Radical Polymerization of M1 to M4. Free radical polymerization of the monomers **M1** to **M4** to obtain linear homopolymers was performed in bulk and in various solvents (Tables 1 and 2). As a typical procedure, **M1** (0.20 g, 0.4 mmol), [1-Me-3-Etim]$N(CF_3SO_2)_2$ (0.20 g), and AIBN (0.003 g, 1.5 wt %) were gently mixed in a flask. The solution was transferred into a glass ampule. After triple freeze−thaw−pump cycles the ampule was sealed under vacuum and heated to 60 °C. The polymerization was carried out at 60 °C for 9 h. The resultant transparent highly viscous polymer solution was slightly diluted with acetone and precipitated into ethyl acetate. **PIL1** was then thoroughly washed with ethyl acetate and dried at 80 °C/1 mmHg for 48 h. Yield: 0.10 g (50%); $\eta_{inh\ DMF}$ = 2.69 dL/g (25.0 °C).

The free radical polymerization of other ILMs was carried out similarly with the exception that the highly viscous solutions of the hydrophilic **PIL3** and **PIL4** were diluted with methanol and precipitated in chloroform.

Typical Procedure for the Free Radical Copolymerization of M1/M3 and M2/M4. Free radical copolymerization of **M1**/**M3** and **M2**/**M4** was performed in accordance with the procedure described for the synthesis of homo-PILs. A typical composition was as follows: **M2** (0.31 g, 0.63 mmol), **M4** (0.20 g, 0.63 mmol), AIBN (0.005 g, 1 wt %), and ethanol (0.5 g). After the completion of the reaction, it was diluted with ethanol and then precipitated into an excess of acetone. The **coPIL1/PIL3** was washed with acetone and dried at 80 °C/1 mmHg for 48 h. Yield: 0.19 g (38%). η_{inh}(0.5 M aq NaCl) = 0.24 dL/g (25.0 °C).

The copolymer **coPIL2/PIL4** was extracted in a Soxhlet apparatus with acetone for 24 h. Then it was dried in a vacuum oven containing a Petri dish with P_2O_5 at 80 °C/1 mmHg for 48 h. Anal. Calcd for $3(C_{11}H_{17}N_2O_2C_7H_{11}SO_5)\cdot 2H_2O$ (1285.5): C, 50.45%; H, 6.90%; N, 6.54%; S, 7.48%. Found: C, 50.36%; H, 6.63%; N, 6.71%; F, 0.00%. IR (KBr pellet): 3100 (m), 2957 (m), 2930 (m), 2915 (m), 2849 (w), 1724 (vs, $\nu_{C=O}$), 1571 (m), 1461 (s), 1385 (w), 1351 (w), 1271 (s), 1189

Table 1. Free Radical Polymerization of M1[a]

					PIL1	
no.	[AIBN] (wt %)	[**M1**] (wt %)	time (h)	solvent	yield (%)	η_{inh} (dL/g)[b]
1	3	100	9		—[c]	—[c]
2	3	50	9	cyclohexanone	67	0.33
3	3	50	9	ethanol	71	1.00
4	3	50	9	1,2-dichloroethane	75	0.71
5	3	50	9	HFIP	47	0.76
6	3	50	9	[N-Me-N-EtPyrr] $N(CF_3SO_2)_2$	53	1.35
7	3	50	9	[1-Me-3-Etim]$N(CF_3SO_2)_2$	81	3.12
8	0.5	50	9	[1-Me-3-Etim]$N(CF_3SO_2)_2$	85	4.64
9	1	50	9	[1-Me-3-Etim]$N(CF_3SO_2)_2$	78	4.06
10	1.5	50	9	[1-Me-3-Etim]$N(CF_3SO_2)_2$	80	3.74
11	3	50	3	[1-Me-3-Etim]$N(CF_3SO_2)_2$	77	3.03
12	3	50	6	[1-Me-3-Etim]$N(CF_3SO_2)_2$	78	2.90
13	3	50	12	[1-Me-3-Etim]$N(CF_3SO_2)_2$	77	3.23
14	3	33	9	[1-Me-3-Etim]$N(CF_3SO_2)_2$	77	2.61
15	3	20	9	[1-Me-3-Etim]$N(CF_3SO_2)_2$	73	2.18
16[d]	0.5	50	9	[1-Me-3-Etim]$N(CF_3SO_2)_2$	75	3.00

[a] T = 60 °C. [b] For the solution of 0.05 g of **PIL1** in 10.0 mL of DMF at 25.0 °C. [c] Insoluble polymer. [d] DCPD was used as initiator, T = 40 °C.

Table 2. Free Radical Polymerization of M3[a]

					PIL3	
no.	[AIBN] (wt %)	[**M3**] (wt %)	time (h)	solvent	yield (%)	η_{inh} (dL/g)[b]
1	3	100	9		—[c]	—[c]
2	3	50	9	cyclohexanone	78	3.55
3	3	50	9	ethanol	73	1.78
4	3	50	9	DMF	35	0.55
5	3	50	9	1,2-dichloroethane	37	2.33
6	3	50	9	1,1,2,2-tetrachloroethane	68	4.84
7	3	50	9	[N-Me-N-EtPyrr] $N(CF_3SO_2)_2$	—[c]	—[c]
8	3	50	4	[N-Me-N-EtPyrr] $N(CF_3SO_2)_2$	—[c]	—[c]
9	3	50	2	[N-Me-N-EtPyrr] $N(CF_3SO_2)_2$	—[c]	—[c]
10	3	30	2	[N-Me-N-EtPyrr] $N(CF_3SO_2)_2$	—[c]	—[c]
11	3	50	9	HFIP	70	4.95
12	1	50	12	HFIP	72	5.25
13	1	33	12	HFIP	73	3.41
14	1	20	12	HFIP	72	2.04
15	0.5	50	9	HFIP	71	6.15
16	1	50	9	HFIP	70	5.96
17	3	50	3	HFIP	72	4.78
18	3	50	6	HFIP	74	4.70
19	3	50	12	HFIP	77	3.79

[a] T = 60 °C. [b] For the solution of 0.05 g of **PIL3** in 10.0 mL of methanol at 25.0 °C. [c] Insoluble polymer.

(vs, RSO_3, ν_{asSO_2}), 1036 (vs, RSO_3, ν_{sSO_2}), 870 (w), 792 (w), 760 (w), 729 (m), 611 (s, RSO_3, ν_{S-O}), 518 (m) cm^{-1}. η_{inh}(0.5 M aq NaCl) = 0.41 dL/g (25.0 °C).

Typical Procedure for the Copolymerization of M1 to M4 with PEGDM. The cross-linked polymer films were prepared as follows. **coPIL/PEGDM**: 0.114 g of PEGDM and 0.228 g of the corresponding ILM were dissolved in 0.4 mL of the respective solvent (cyclohexanone for **M1** and **M2**, 1,1,2-trichloroethane for **M3** and **M4**) at 20 °C under an inert gas. Cross-linked terpolymer **coPILn/PILm/PEGDM**: 0.114 g of **PEGDM**, 0.138 g (0.28 mmol) of **M1** or **M2** and 0.090 g (0.28 mmol) of **M3** or **M4** were dissolved in 0.4 mL of 1,1,2-trichloroethane at 20 °C under an inert gas. 0.0103 g of AIBN (3 wt %) were added, and the mixture was thoroughly stirred until the formation of a clear solution, which was poured into a mold made from two glass plates clamped together and sealed with a 500 μm thick Teflon gasket. Afterward, the mold was kept at 60 °C for 15 h. The resultant film was taken out from the mold at ambient temperature and was then dried at 60 °C for 3 h and finally for 10 h at 80 °C/1 mmHg.

Film Casting from Linear PILs. **PIL1** to **PIL4**, **coPIL1/PIL3**, and **coPIL2/PIL4** films were cast from 5 wt % polymer solutions (**PIL1**, **PIL2** from acetone, **PIL3**, **PIL4** from methanol, and **coPIL1/PIL3**, **coPIL2/PIL4** from HFIP) directly on the golden electrode's surface. The solvent was slowly evaporated at 50 °C. The obtained thin polymer coatings together with electrodes were dried at 80 °C/1 mmHg for 24 h.

Methods. NMR spectra were obtained on Bruker AMX-300 and Bruker AMX-400 spectrometers at 25 °C in the indicated deuterated solvent and are listed in ppm in the ionic liquids section above. The signal corresponding to the residual protons of the deuterated solvent was used as an internal standard (^{1}H, ^{13}C relative to tetramethylsilane), and $CHCl_2F$ was used as an internal standard for ^{19}F NMR. A Nicolet Magna-750 Fourier IR-spectrometer was used to record IR spectra at a resolution of 2 cm^{-1} and with the scan number equal to 128 (KBr pellets).

Inherent viscosities (η_{inh}) were measured using an Ostwald capillary viscometer (0.05 g of polymer in 10.0 mL of solvent at 25.0 °C), while the intrinsic viscosities $[\eta]$ were determined in Ubbelohde-type capillary viscometer at 25.0 °C.

The average $\overline{M}_{sD}$ polymer molar masses were determined at 25.0 °C in 0.5 M $Li(CF_3SO_2)_2N$ solution in DMF for **PIL1** and **PIL2** and at 20.0 °C in 0.5 M aq NaCl for **PIL3** and **PIL4** by sedimentation–diffusion analysis. The density and viscosity of the 0.5 M $Li(CF_3SO_2)_2N$ solution in DMF were determined as $\rho_0 = 1.25$ g/cm^3 and $\eta_0 = 1.0208$ cP while the appropriate values for 0.5 M aq NaCl were $\rho_0 = 1.019$ g/cm^3 and $\eta_0 = 1.052$ cP. Sedimentation velocity was performed in an analytical ultracentrifuge (ProteomeLab XLI Protein Characterization System, Beckman Coulter Inc.) at a rotor speed of 40 000 rpm. The buoyancy factor $(1 - \upsilon\rho_0)$ and the partial specific volumes υ (0.690, 0.685, 0.785, and 0.757 mL/g for **PIL1-PIL4**, respectively) were obtained by densitometery using a DMA-4000 densitometer (Anton Paar GmbH, Austria).

The glass transition temperature (T_g) of the linear PILs was determined by thermomechanical analysis (TMA) using a UIP-70 M (Russia) thermomechanical analyzer at a heating rate of 2.5 °C/min and a constant load of 0.08 MPa. Dynamic mechanical thermal analysis (DMTA) measurements were carried out on copolymer (coPILs) films (typically length × width × thickness = 15 × 8 × 0.5 (mm)) with a Q800 model (TA Instruments) operating in tension mode (strain between 0.05% and 0.07%; pretension: 10^{-2} N). Experiments were performed at 1 Hz frequency with a heating rate of 3 °C/min from −90 to +150 °C. The setup provided the storage and loss modules (E' and E''). The damping parameter or loss factor (tan δ) was defined as the ratio $\tan \delta = E''/E'$. Thermogravimetric analysis (TGA) was performed in air on a Q50 model (TA Instruments) applying a heating rate of 5 °C/min. Differential scanning calorimetry (DSC) measurements were carried out on a DSC Q100 (TA Instruments) from −90 to 40 °C at a heating rate of 2 °C/min.

The efficiency of cross-linking reactions between the ILMs and **PEGDM** was estimated by the extraction of the copolymer films in a Soxhlet apparatus with dichloromethane for 10 h with subsequent drying in vacuum at 80 °C overnight.

Dielectric spectroscopy studies of monomers, PILs, and coPIL's films were run on a Novocontrol broadband dielectric spectrometer equipped with an Alpha analyzer and a Quatro temperature controller (Novocontrol GmbH, Germany). The films were preliminarily dried in a vacuum oven containing a Petri dish with P_2O_5 at 80 °C/1 mmHg and then sandwiched between gold-coated brass electrodes. The experiments were carried out at 25 °C in 10^{-1}–10^7 Hz frequency range in air. In all cases conductivity results were duplicated with a complex impedance method using an impedance analyzer Autolab PGSTAT30 (Autolab Frequency Response Analyzer System, Metrohm Autolab B.V., The Netherlands). The runs were performed in air varying the frequency from 10^{-2} to 10^8 Hz at 25 °C. A polymer film was put in a cell with pressure contact stainless steel electrodes.

The ionic conductivity of three copolymers, namely **coPIL1/PEGDM**, **coPIL3/PEGDM**, and **coPIL1/PIL3/PEGDM**, was measured at various relative humidity (RH). To achieve good electrical contact, both surfaces of the polymer films were sputtered with gold using a sputter coater (BAL-TEC SC005, Tucson, AZ). This procedure yielded small gold electrodes of 10 mm in diameter and with thickness of about 20 nm, as monitored by a quartz crystal oscillator. The sputtered polyelectrolyte films were stored over $Ca(CO_3)_2$ in a dry room for about 4 days prior to measurements and transfer to a humidity chamber (Memmert constant chamber HPP1087749 with Peltier Technology, Memmert GmbH & Co, Germany). All three investigated samples were simultaneously exposed to the air with the given humidity. The measurements were carried out at 25 °C and varying relative humidity of the chamber from 20% to 60% in steps of 10%. The RH was measured via a hygrometer (PCE-555, PCE-Group, Meschede) with an error of ±0.5%. At a given humidity, the measurements were performed until a constant dc conductivity value was observed, which assured full equilibration of the sample. Conductivity spectra were recorded with an impedance analyzer (hp 4192 A, Hewlett-Packard Co.) covering a frequency range from 5 to 1.3 × 10^7 Hz.

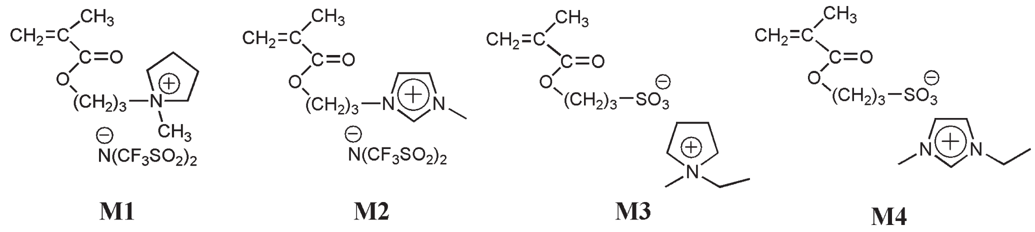
RESULTS AND DISCUSSION

Monomer Synthesis and Characterization. The design of the ionic liquid like monomers **M1** to **M4** (Scheme 2) was developed taking into account the previously established relationships between the monomer structure and the ionic conductivity of the respective polymer.[3,4] As it was demonstrated previously,[22,23] the methacrylate functional group offers higher reactive ability for the respective ILMs and allows for the formation of polymers with higher molar masses in comparison with the quaternized *N*-vinylimidazoles. The ionic center was placed on the end of a flexible alkyl side chain. Imidazolium and pyrrolidinium cations were chosen because the first one offers the highest ionic conductivity for the respective imidazolium-based ILs, while the second cation provides good electrochemical stability.[24] In its turn, the bis(trifluoromethylsulfonyl)amide anion is characterized by high delocalization of the negative charge, low basicity, and good mobility.[24] To avoid any confusion, we have elected to use the terms "cationic" ILMs for **M1** and **M2** because of the corresponding polycations formation and "anionic" monomers for **M3** and **M4** throughout this paper.

Two synthetic pathways for the preparation of polycationic bis(trifluoromethylsulfonyl)amide containing ILMs **M1** and **M2** differing by the sequence of the performed reactions were reported previously.[8,11,25] In contrast, methods for the preparation of anionic ILMs with noncovalently bonded quaternized cations have not been studied. Here, two new anionic ILMs (Scheme 2, **M3** and **M4**) have been prepared via ion exchange reaction from commercially available 3-sulfopropyl methacrylate potassium salt and corresponding quaternary ammonium chlorides.

The elaboration of a method for anionic **M3** and **M4** synthesis faced several problems. The first one rose from the insolubility of the initial 3-sulfopropyl methacrylate potassium salt in common organic solvents. The application of water as a solvent was unacceptable because of the complexity of monomer isolation and possibility of their spontaneous polymerization. The solution was found in the utilization of acetonitrile containing small traces of water (ca. 0.5 wt %) which was capable to dissolve the starting potassium salt in contrast to dry acetonitrile. At that, the drier was the solvent, the better was the precipitation of the byproduct (KCl). It was revealed that the reaction between

Scheme 2. Chemical Structure of Ionic Liquid-like Monomers Used in This Study



the equimolar amounts of the respective chloride ILs and the 3-sulfopropyl methacrylate potassium salt proceeds quantitatively, while the utilization of bromide ILs leads to the mixture of products. The structure and purity of **M1** to **M4** were proved by NMR and IR spectroscopy and elemental analysis.

It should be noted, that upon the preparation, isolation and subsequent drying of **M1** to **M4** the addition of respective inhibitors, for example 4-methoxyphenol, was necessary to avoid spontaneous radical polymerization. Without any radical inhibitor, the partial oligomerization of **M3** and **M4** was observed upon their storage under inert atmosphere even at ambient temperature. The cationic ILMs **M1** and **M2** were found to be more stable toward spontaneous oligomerization in comparison with anionic **M3** and **M4**.

The thermal behavior of all four monomers was investigated by DSC. The DSC diagrams made even with a slow rate of 2 °C/min revealed no crystallization or melting processes for the studied ionic compounds, in contrast to the initial 3-sulfopropyl methacrylate potassium salt (mp 295 °C). Only T_g were observed for all monomers. Practically no difference was found for T_g of the respective pairs of monomers: **M1** (−67.1 °C) and **M2** (−68.1 °C), **M3** (−75.9 °C) and **M4** (−71.2 °C). The general tendency[5] that the melting points of pyrrolidinium-based ILs are higher than of their imidazolium analogues was not confirmed here. Instead, the anionic monomers **M3** and **M4** had lower glass transition temperatures then their cationic analogues **M1** and **M2**.

As a result of the ionic conductivity investigation, the following order of ILMs conductivity at 25 °C was obtained: **M2** > **M1** > **M4** > **M3** with values of $1.2 \times 10^{-3} > 7.7 \times 10^{-4} > 6.1 \times 10^{-4} > 9.7 \times 10^{-5}$ S/cm.

The difference in the ionic conductivity of respective monomer pairs, **M1** and **M3**, **M2** and **M4**, does not exceed 1 order of magnitude. However, cationic monomers containing small bis(trifluoromethylsulfonyl)amide anion are more conductive than their anionic analogues with bulky heterocyclic cations. The fact that the anionic **M1** and **M2** monomers demonstrated better conductivity than **M3** or **M4** can also be explained by the difference in viscosity, since all liquid cationic ILMs are more viscous than the anionic ones. According to the common tendency, the imidazolium-based ionic monomers have higher conductivity than pyrrolidinium ones.[5,24,25]

Free Radical Polymerization of ILMs. As was demonstrated previously, the properties of PILs depend on the molar mass of the polyelectrolyte.[25] Taking this into account, initially it was important to prepare polymers of high molar mass from **M1** to **M4**. Herein, the free radical polymerization of cationic **M1** and anionic **M3** was studied exemplarily, and the optimal conditions for the preparation of high molar mass polyelectrolytes were elaborated (Tables 1 and 2).

Most frequently, bulk polymerization yields polymers with higher molar masses than solution polymerization.[26] Thus, the free radical polymerization of **M1** and **M3** was performed in bulk and initiated by AIBN (Table 1, entry 1; Table 2, entry 1). Unexpectedly, the bulk polymerization of both cationic **M1** and anionic **M3** produced polymers which were insoluble in common organic solvents.

It was reported that, in contrast to nonionic unsaturated monomers, ILMs successfully polymerize in ethanol.[2,4] Simultaneously, it was revealed that cyclohexanone dissolves many of the ionic monomers and can serve as a good solvent for ILMs free radical polymerization process.[22] It even sometimes plays the role of a co-initiator.[27] HFIP was recently reported as a perspective solvent for living ATRP of 1-adamantyl methacrylate.[28] ILs were successfully used for the synthesis of high molecular weight polymers via free radical polymerization of both nonionic unsaturated monomers[23,29−34] and some ILMs.[9,23,25] The choice of $[1\text{-Me-3-Etim}](CF_3SO_2)_2N$ and $[N\text{-Me-N-EtPyrr}]\ N(CF_3SO_2)_2$ ionic liquids as the reaction medium for the **M1** polymerization was governed by the availability of the similar bis(trifluoromethylsulfonyl)amide anions; otherwise, any other free anions in the reaction mixture will lead to undesirable ionic exchange between the monomer, solvent, and the resultant polymer.[9] By the same reasons, for the polymerization of anionic **M3**, the $[N\text{-Me-N-EtPyrr}]\ N(CF_3SO_2)_2$ containing pyrrolidinium cation was taken.

Polycationic **PIL1** with the highest yield (81%) and the highest molar mass ($\eta_{inh,DMF} = 3.12$ dL/g) was obtained in $[1\text{-Me-3-Etim}](CF_3SO_2)_2N$ ionic liquid (Table 1, entry 7). The utilization of traditional organic solvents decreased both the molar mass of **PIL1** and its yield (Table 1, entries 2−5). The superior results for the formation of polycations in the ionic reaction medium can be explained by the same factors as for the successful polymerization of nonionic monomers in ionic liquids.[29,31,32,35,36]

In contrast to polycations, the highest yields (68−70%) and η_{inh} for the polyanionic **PIL3** were reached in organic solvents, namely, 1,1,2,2-tetrachloroethane and HFIP (Table 2, entries 6, 11, and 2−5). The implementation of the ionic solvent led to the formation of insoluble polymers (Table 2, entries 7−10). This can possibly be attributed to the formation of polyanions with extra high molar mass or to the generation of some highly ordered polymer network via the physical interaction of polyelectrolyte chains with ILs.[37−39]

As was shown previously, the nature of the initiator can play an important role for the accomplishment of ILM's free radical polymerization.[3,22,25] Table 1 (entries 8 and 16) proves the efficiency of AIBN and DCPD initiators for the polymerization of cationic **M1**. AIBN was also effective for the polymerization of anionic **M3** (Table 2), while DCPD did not provide high molar mass **PIL3**. The discoloration from light green to light blue and finally to bright yellow was observed upon the dissolution of DCPD in **M3**/ethanol solution, which was probably due to the formation of side complexes. The variation of the initiator concentration from 0.5 to 3 wt % gave similar relations for the polymerization of both cationic **M1** and anionic **M3**. The increase of the AIBN concentration resulted in a decrease of η_{inh} for **PIL1** from 4.64 to 3.12 dL/g (Table 1, entries 7−10) and for **PIL3** from 6.15 to 4.95 dL/g (Table 2, entries 11, 15, and 16).

The decrease of the monomer concentration from 50 to 20 wt % was reducing the polycation inherent viscosity from 3.12 to 2.18 dL/g (Table 1, entries 7, 14, and 15). Simultaneously, a slight decrease of the yield of cationic **PIL1** from 81 to 73% was observed. The same tendency was noticed during the gradual change of anionic **M3** concentration (Table 2, entries 12−14). The inherent viscosity dropped down from 5.25 to 2.04 dL/g; however, the **PIL3** yield was very similar in the range 70−73%.

For the cationic **M1** polymerization, increased reaction time only slightly influenced the molar mass, which was monotonously rising (Table 1, entries 7, 11−13). As for anionic **PIL3** the time dependence of the molar mass was passing through a maximum (Table 2, entries 11, 17−19). The highest value of the $\eta_{\text{inh,MeOH}}$ = 4.95 dL/g was observed for the polyanion isolated after 9 h of reaction (Table 2, entry 11).

The free radical polymerization studies (Tables 1 and 2) allowed for identifying the optimal reaction conditions for the synthesis of polycations and polyanions with high molar masses and in high yields. The optimal AIBN concentration (0.5 wt %), monomer concentration ([solvent]/[M] = 1:1 by wt), and the reaction time (∼6 h) were found to be very similar for the synthesis of both polycations and polyanions. However, the reaction medium was different. For the polycations **PIL1** and **PIL2**, the best solvent was the [1-Me-3-Etim]$(CF_3SO_2)_2N$ ionic liquid, while for the polyanions **PIL3** and **PIL4**, the best reaction medium was HFIP.

The copolymerization of the oppositely charged monomers **M1**/**M3** and **M2**/**M4** was carried out applying the established optimized reaction conditions. Ethanol was chosen as a solvent to prevent any ion exchange reaction (in comparison with ILs as reactive medium) and to simplify the estimation of the copolymer composition by the content of fluorine. It was revealed that, due to the necessary precipitation of the copolymer, the major part (∼70%) of the noncovalently bonded ions was removed. The further continuous extraction of the **coPIL1/PIL3** and **coPIL2/PIL4** copolymers with acetone led to the loss of all remained mobile counterions and to the formation of polyampholytes. Subsequently, copolymers that do not contain mobile counterions will be designated as "extracted" **coPIL1/PIL3** or **coPIL2/PIL4**. One can ask an appropriate question of how much free is IL inside the copolymer and what is its state. Ordinarily, considering polyelectrolytes it is believed that between the ions integrated in the polymer backbone and the counterions there is an ionic bond as in low molar mass salts. According to the elemental analysis, the obtained copolymers are polyampholytes with nearly balanced ratio between the oppositely charged monomer units. The synthesis of such polyampholytes is performed in solution; thus, the dissociation and the subsequent ion exchange reactions happen between all ions. After the isolation of the copolymers through the precipitation method mixed interactions are present. Some of the counterions are still ion bonded to their "native" pairing ions that are chemically attached to the polymer chain. Some of the chemically bonded to the polymer chain ions started to interact with the oppositely charged covalently bonded ions. And finally, some of the counterions diffuse and associate into the ILs molecules and will be present inside the polyampholytes due to the electrostatic interactions with covalently bonded ions. These ILs molecules are randomly and homogeneously distributes inside the copolymer matrix. Because of the electrostatic interactions, they are only weakly connected to the copolymer and thus can be fully extracted with solvents. However, neither the rise of the temperature nor the application of pressure to the polyampholyte films led to the sweating or isolation of free liquid ILs.

Table 3. Solubility of PIL1, PIL3, and Copolymer coPIL1/PIL3[a]

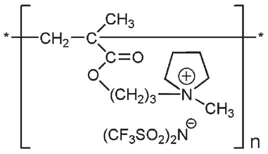
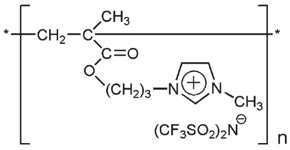
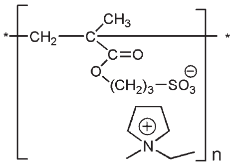
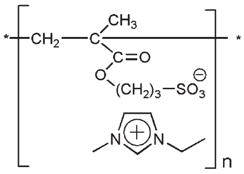
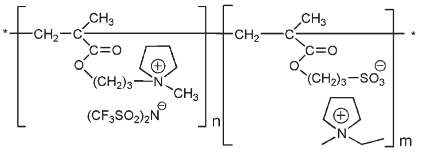
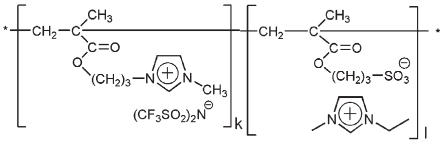
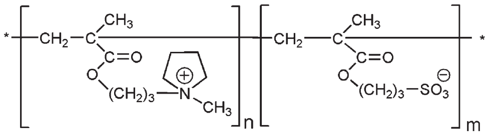
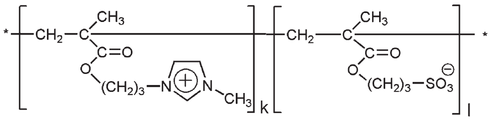
	polymer		
solvent	PIL1	PIL3	coPIL1/PIL3[b]
DMF	+	−	−
0.5 M LiCl in DMF	−	+	+[t]
0.5 M $Li(CF_3SO_2)_2N$ in DMF	+	−	−
DMSO	+	+[t]	−
NMP	+	−	−
HMPA	+	−	−
H_2O	−	+	+
0.5 M NaCl in H_2O	−	+	+
methanol	−	+	−
HFIP	+	+[c]	+
acetone	+	−	−
1,2-dichloroethane	+	−	−
chloroform	−	−	−
diethyl ether	−	−	−
sym-tetrachloroethane/phenol (3:1, by wt)	+[t]	−	−

[a] Solubility: (+) soluble at ambient temperature, (+[t]) soluble on heating to 60 °C, (−) insoluble even on heating. [b] Extracted copolymer.

Solution Properties of the PILs. The solubility of **PIL1**, **PIL3**, and extracted **coPIL1/PIL3** presents remarkable differences (Table 3). The bis(trifluoromethylsulfonyl)amide anions impart the hydrophobicity and improve the solubility of the polycations in solvents such as DMF, DMSO, NMP, acetone, and 1,2-dichloroethane. **PIL1** and **PIL2** are insoluble in water or aqueous salt solutions, in contrast to their polycationic analogues containing the chloride anion.[40,41] Interestingly, **PIL1** is soluble in HMPA at ambient temperature but precipitates upon heating to 60 °C, indicating the phenomenon of a critical solution temperature. The synthesized polycations are insoluble in chloroform, diethyl ether, and methanol. However, HFIP, probably due to the fluorinated nature of the bis(trifluoromethylsulfonyl)-amide anion, was capable to dissolve both **PIL1** and **PIL2**. On the contrary, solubility was observed for polyanions (Table 3). Polymers prepared from anionic **M3** and **M4** are readily soluble in water, aqueous salt solutions, and alcohols. In contrast to polycations, the **PIL3** is not soluble in DMF, NMP, or HMPA. To dissolve anionic **PIL3** or **PIL4** in DMF, the addition of inorganic salt was necessary. **PIL3** was found to be insoluble in acetone, diethyl ether, and chlorinated solvents such as chloroform, dichloromethane, and 1,2-dichloroethane. The solubility of extracted polyampholyte **coPIL1/PIL3** was lower than that of the respective homopolymers (Table 3). Among the tested solvents, only water, aqueous salt solutions, and HFIP were able to dissolve **coPIL1/PIL3** at ambient temperature.

Because of insufficient electrostatic screening, the determination of [η] was not possible for **PIL1** in pure DMF. To achieve

Table 4. Physicochemical Properties of PIL Homo- and Copolymers

no	sample	polymer	η_{inh} (dL/g)[a]	[η] (dL/g)[b]	M_{sD} (g/mol)[c]	T_g (°C)[d]	σ_{DC}, (S/cm)[e]	T_d (°C)[f]
1	**PIL1**		2.69	0.40	1.24×10^6	55	7.8×10^{-9}	305
2	**PIL2**		2.60	0.52	1.04×10^6	16	3.1×10^{-8}	330
3	**PIL3**		5.25	1.49	2.55×10^6	63	3.3×10^{-10}	265
4	**PIL4**		3.70	1.02	1.22×10^6	40	3.2×10^{-8}	295
		copolymers as obtained						
5	**coPIL1/PIL3**		0.42	-	-	38	9.7×10^{-12}	275
6	**coPIL2/PIL4**		0.24	-	-	34	1.1×10^{-8}	270
		copolymers after the extraction with acetone						
7	**coPIL1/PIL3**		0.49	0.51	-	153	4.1×10^{-12}	255
8	**coPIL2/PIL4**		0.41	0.42	-	45	5.6×10^{-10}	220

[a] For the solution of 0.05 g of polymer in 10.0 mL of DMF (**PIL1**, **PIL2**), methanol (**PIL3**, **PIL4**) or 0.5 M aq NaCl (**coPIL1/PIL3**, **coPIL2/PIL4**) at 25.0 °C. [b] For the solution of polymer in 0.5 M $Li(CF_3SO_2)_2N$ in DMF (**PIL1**, **PIL2**) or 0.5 M aq NaCl (**PIL3**, **PIL4**, extracted **coPIL1/PIL3**, **coPIL2/PIL4**) at 25.0 °C. [c] Determined by sedimentation−diffusion analysis in 0.5 M $Li(CF_3SO_2)_2N$ in DMF (**PIL1**, **PIL2**) or 0.5 M aq NaCl (**PIL3**, **PIL4**, extracted **coPIL1/PIL3**, **coPIL2/PIL4**). [d] By thermomechanical method. [e] Ionic conductivity of polymer film at 25 °C. [f] Onset loss temperature according to TGA.

sufficient screening, $Li(CF_3SO_2)_2$,which contains the native anions of the polycation, was added to DMF. The use of 0.5 M $Li(CF_3SO_2)_2$ in DMF as solvent yielded the intrinsic viscosities 0.40 and 0.52 dL/g for **PIL1** and **PIL2**, respectively (Table 4, entries 1 and 2).

For anionic **PIL3** and **PIL4** polyelectrolyte effects were observed in methanol and in water, while the use of 0.5 M aqueous NaCl as solvent gave an intrinsic viscosity value of 1.49 dL/g for **PIL3** (Table 4, entry 3) and $[\eta]$ = 1.02 dL/g for **PIL4** (Table 4, entry 4). Appropriately, for the extracted copolymers **coPIL1/PIL3** and **coPIL2/PIL4** intrinsic viscosities of 0.51 and 0.42 dL/g were obtained (Table 4, entries 7 and 8).

The molar masses of the polyelectrolytes were estimated by sedimentation−diffusion analysis in solvents where polyelectrolyte effects were suppressed. The M_{sD} of both the cationic and anionic PILs were found to be in the range of 10^6 g/mol (Table 4, entries 1−4). The molar masses of anionic **PIL3** and **PIL4** are higher than of cationic **PIL1** and **PIL2**. This allows concluding that the respective **M3** and **M4** monomers are more reactive than their cationic analogues, probably due to the more bulkiness of the cationic monomers.

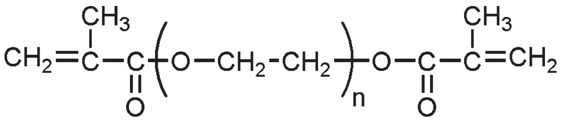
Properties of PILs Films. From all synthesized high molar mass PILs and their copolymers free-standing tight films could be produced. However, the hydrophilicity of **PIL3** and **PIL4** and of extracted **coPIL1/PIL3** and **coPIL2/PIL4** represented some problems. To exclude the influence of water, all measurements were performed either under inert atmosphere or on as dry samples as it was possible (Table 4).

As it was previously demonstrated, the molar mass of the PIL greatly influences both its bulk ionic conductivity and T_g.[3,25] However, above a certain degree of polymerization the ionic conductivity leveled off, and no further changes were observed. Such critical point was found to be equal to $M_{sD} \sim 3.50 \times 10^5$ g/mol for methacrylate-based PIL bearing bis(trifluoromethylsulfonyl)amide anions.[25] The molar masses determined for **PIL1**−**PIL4** are in the range of 10^6 g/mol (Table 4). Therefore, their conductivity should not be dependent on the molar mass. The ionic conductivity of polycation **PIL1** was found to be 7.8×10^{-9} S/cm at 25 °C (Table 4, entry 1), while for polyanion **PIL3** σ reached the value of 3.3×10^{-10} S/cm, which is lower by more than 1 order of magnitude (Table 4, entry 3). This can be explained by poor dissociation of the bulky pyrrolidinium cation and inactivated SO_3^- groups in comparison to the small and highly delocalized $(CF_3SO_2)_2N^-$ anion. The transfer to the imidazolium PILs resulted in the coincidence of the ionic conductivity values for the corresponding polycation **PIL2** and polyanion **PIL4** (Table 4, entries 2 and 4). Probably, the reason for this findings is the higher delocalization degree of the aromatic imidazolium cation. The increase in the cation's delocalization can lead to the increase of the dissociation of **PIL4** in comparison with **PIL3**. As a conclusion, pyrrolidinium-based linear PILs are less conductive than imidazolium ones, which is in agreement with the reported tendency for comparable ILs.[5,24] The partial loss of the mobile counterions during the isolation of the copolymers **coPIL1/PIL3** and **coPIL2/PIL4** led to the decrease of their ionic conductivity in comparison with the corresponding homopolyelectrolytes (Table 4, entries 5, 6, and 1−4). The complete removal of the mobile ions from the **coPIL1/PIL3** and **coPIL2/PIL4** resulted in a considerable drop of the ionic conductivity to 4.1×10^{-12} and 5.6×10^{-10} S/cm, respectively (Table 4, entries 7 and 8).

The glass transition temperatures of linear PILs were determined by the TMA method (Table 4). The T_g of all studied polyelectrolytes exceeds 25 °C (Table 4, entries 1 and 3−8). The only exception was the **PIL2** having a T_g = 16 °C (Table 4, entry 2). The data in Table 4 demonstrate that the decrease of T_g of the homopolymer leads to the increase of its ionic conductivity at 25 °C (Table 4, compare 1 and 2, 3 and 4). This tendency agrees with previously published data.[2−4] As expected, the loss of the mobile counterions converted the ionic copolymers into polyampholytes and increased their T_g (Table 4, entries 5 and 7, 6 and 8).[2] The values of T_g allowed to conclude that polycations possess lower T_g than respective polyanions.

Thermal stability studies by TGA yielded the onset temperature of degradation. The bis(trifluoromethylsulfonyl)amide anion imparts the high thermal stability to the respective polycations increasing their T_d over 300 °C (Table 4, entries 1 and 2) that is in a agreement with previously published data.[2−4] Compared to polycations **PIL1** and **PIL2**, a decrease of the onset loss temperature was observed for polyanions **PIL3** and **PIL4** (Table 4, entries 1−2 and 3−4). **coPIL1/PIL3** and **coPIL2/PIL4** had T_d either lower (Table 4, entries 2, 4, and 6) than the corresponding homopolymers or in between the respective polycation and polyanion (Table 4, entries 1, 3, and 5). The conversion into extracted copolymers led to further reduction in thermal stability (Table 4, entries 5 and 7, 6 and 8).

Scheme 3. Chemical Structure of PEGDM



$CH_2{=}C(CH_3){-}C({=}O){-}(O{-}CH_2{-}CH_2)_n{-}O{-}C({=}O){-}C(CH_3){=}CH_2$

PEGDM (n = 13-14)

Copolymers of M1 to M4 with PEGDM. The copolymerization of ILMs with monomers containing PEO fragments represents one of the approaches to improve the PIL's ionic conductivity and to reduce of the T_g.[2,4,7,13,22,25] **PEGDM** was previously found to be a promising candidate for the copolymerization with ionic monomers.[7,13,22,25]

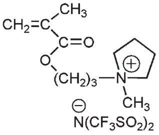
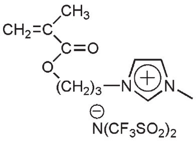
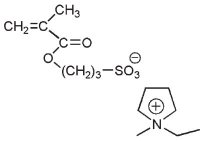
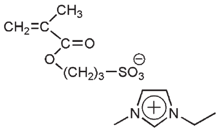
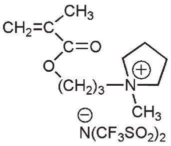
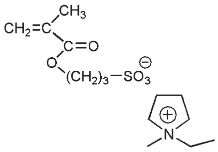
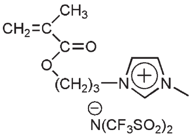
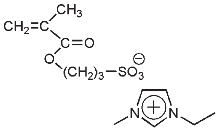
Terpolymerization of **PIL1**, **PIL3**, and **PEGDM** was also supposed to prevent the loss of mobile counterions and to avoid the precipitation process prior to the preparation of the polyelectrolyte films. **M1**−**M4** were copolymerized with **PEGDM** using the previously determined optimal ratio.[22,25] Both the co- and terpolymerization resulted in transparent, tight, and elastic films (Table 5).

To determine the T_g of the films and to confirm the formation of a single phase network, the DMTA method was utilized (Figure 1). The homopolymerization of **PEGDM** yielded elastic films with low T_g (T_α more correctly) equal to −23 °C (Figure 1, curve 1). Figure 1 demonstrates that for all copolymer films single relaxation peaks were observed that, in its turn, proved the formation of the single networks at least at the DMTA measurements scale. According to the tan δ vs temperature dependence (Figure 1, curves 2 and 3), the copolymer of **PEGDM** with **M4**, i.e. polyanion network, had a lower T_g value (−4.1 °C) in comparison with cationic **coPIL2/PEGDM** (T_g = 8.9 °C).

The maximum of tan δ for terpolymer **coPIL2/PIL4/PEGDM** was observed in between the maxima of **coPIL4/PEGDM** and **coPIL2/PEGDM** (Figure 1, curves 4 and 2, 3), indicating that the terpolymer has an average T_g in comparison with respective copolymers. The same tendency was observed for **coPIL1/PEGDM**, **coPIL3/PEGDM**, and **coPIL1/PIL3/PEGDM** (Table 5, entries 1, 3 and 5). As compared with the corresponding linear PILs (Table 4), the copolymerization of the ionic monomers with **PEGDM** resulted in significant decrease of T_g (Table 5).

The efficiency of cross-linking was estimated by the extraction of **M1** to **M4** and **PEGDM** copolymer films (Table 5). As the soluble fraction content in anionic **coPIL3/PEGDM** and **coPIL4/PEGDM** was low, 1.5 and 1.0 wt %, respectively, it was concluded that the networks obtained were almost completely cross-linked. In contrast, the results of extraction give the evidence that the cationic **coPIL1/PEGDM** and **coPIL2/PEGDM** films are not completely cross-linked (Table 5, entries 1 and 2).[28,31] The soluble fraction was studied by NMR, and it was found that it consisted mainly of nonionic and/or respective linear **PIL1** or **PIL2**.

Table 5. Properties of the M1 to M4 Copolymers and Terpolymers with PEGDM

no	copolymer	ILMs		appearance of the film	σ_{DC}, (S/cm)[a]	T_α, (°C)[b]	T_{onset}, (°C)[c]	Extractable fraction, (wt.%)[d]
1	**coPIL1/PEGDM**		-	slightly yellow transparent	1.0×10^{-6}	8.3	235	16.2
2	**coPIL2/PEGDM**		-	colorless transparent	1.5×10^{-6} [e]	8.9	240	12.9
3	**coPIL3/PEGDM**	-		colorless transparent	1.1×10^{-7}	-4.9	235	1.5
4	**coPIL4/PEGDM**	-		colorless transparent	2.5×10^{-7}	-4.1	245	1.0
5	**coPIL1/PIL3/PEGDM**			yellow transparent	5.4×10^{-6}	4.9	235	-
6	**coPIL2/PIL4/PEGDM**			slightly yellow transparent	4.6×10^{-6}	1.2	240	-

[a] Ionic conductivity of polymer film at 25 °C. [b] By dynamic mechanical thermal analysis (DMTA). [c] Onset loss temperature according to TGA. [d] Films were extracted with CH_2Cl_2 (Soxhlet extraction) for 10 h and subsequently dried at 80 °C under vacuum. [e] $\sigma = 4.0 \times 10^{-6}$ S/cm at 25 °C when the gold was sputtered on the film's surface from both sides for better contact.

TGA of the obtained copolymers revealed almost identical onset loss temperature (235−245 °C) for all copolymer films regardless of the nature of the ionic monomer (Table 5). Generally, the thermal stability of the copolymer films based on **M1** to **M4** and **PEGDM** was lower than that of the respective homopolymers (Tables 4 and 5).

The copolymerization with **PEGDM** resulted not only in lower T_g but also in a remarkable increase of the ionic conductivity. The σ values were found to be $10-10^3$ times higher than that of the respective homopolyelectrolytes (Tables 4 and 5, entries 4, 1 and 3). The investigation of the terpolymers in anaerobic conditions revealed that the **coPIL1/PIL3/PEGDM** and **coPIL2/PIL4/PEGDM** had the highest ionic conductivity among the investigated films. On the one hand, the technology of the preparation of such terpolymers films does not need the precipitation technique, and as a result, the free ILs molecules formed by the dissociation/association during solution polymerization were not washed out. On the other hand, the improvement of the conductivity of the terpolymers in comparison with copolymers (**coPILX/PEGDM**) can only be explained by enhanced ion transport. Upon consideration of terpolymers as a sum of two respective copolymers (**coPILX/PEGDM**) taken in 1:1 ratio, it becomes obvious that the total amount of ions remains the same. Thus, the only difference between the terpolymers and corresponding copolymers (**coPILX/PEGDM**) can be in the mobility of ions. In the mentioned copolymers all the counterions are ion bonded to the ions that are covalently attached to the polymer backbone. As a consequence, the improvement of conductivity for terpolymers can be reached only by the presence of the mobile free ILs molecules inside the polymer matrix. These results demonstrate a clear advantage of terpolymerization of oppositely charged ionic monomers over respective homo- and copolymers (**coPILX/PEGDM**).

According to published data, the polyanions with imidazolium cations demonstrate higher ionic conductivities than the respective polycations.[2,4] This statement was found to be in contradiction with the results obtained herein (Tables 4 and 5). Such difference can be explained by the hydrophilic character of the polyanions and the possibility of the humidity influence on their conductivity. To prove this assumption, additional conductivity

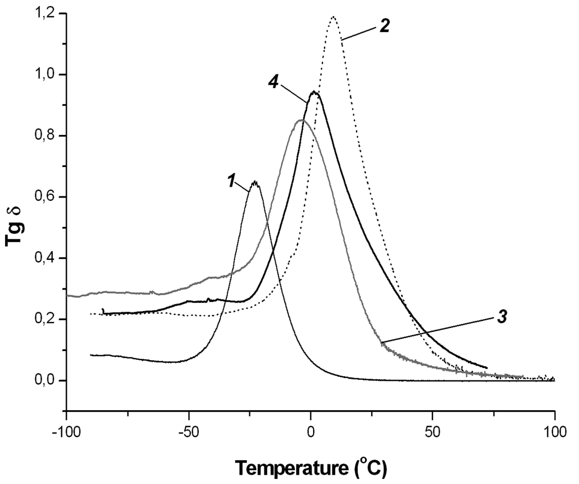


Figure 1. DMTA analysis of polymer films: **PEGDM** film (1), **coPIL2/PEGDM** film (2), **coPIL4/PEGDM** film (3), and **coPIL2/PIL4/PEGDM** film (4).

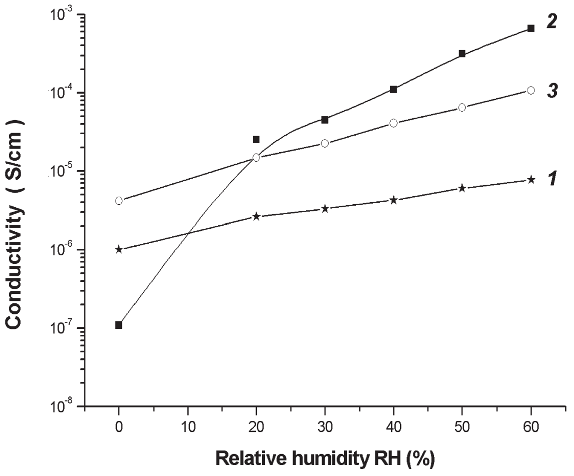


Figure 2. Ionic conductivity of **coPIL1/PEGDM** (1), **coPIL3/PEGDM** (2), and **coPIL1/PIL3/PEGDM** (3) as a function of relative humidity (the lines are guides to the eye).

experiments were carried out varying the relative humidity. Figure 2 demonstrates for **coPIL1/PEGDM**, **coPIL3/PEGDM**, and **coPIL1/PIL3/PEGDM** films that water influences the ionic conductivity. Thus, with the increase in relative humidity the ionic conductivity of the copolymer based on hydrophobic **M1** monotonically raised from 1.0×10^{-6} (dry state) to 7.7×10^{-6} S/cm at RH = 60% (Figure 2, curve 1). The slope of the curve of terpolymer **coPIL1/PIL3/PEGDM** containing hydrophilic **M3** units was higher than that of **coPIL1/PEGDM** (Figure 2, curves 1 and 3). The conductivity of **coPIL1/PIL3/PEGDM** was changing from 5.4×10^{-6} to 1.1×10^{-4} S/cm with the humidity rise to 60%. Finally, the ionic conductivity of the hydrophilic polyanion **coPIL3/PEGDM** was increasing strongly already at low humidity values (Figure 2, curve 2). The change from the anaerobic conditions to 20% of relative humidity resulted in 220-fold increase of the **coPIL3/PEGDM** ionic conductivity, from $\sigma_{\text{dry}} = 1.1 \times 10^{-7}$ to $\sigma_{20\%\ \text{RH}} = 2.5 \times 10^{-5}$ S/cm.

Conductivity studies on PEMs have revealed that the conductivity rises by orders of magnitude if the relative humidity (RH) of the environment is increased.[16−18] PEMs are typically proton conductors, since they contain almost no small mobile ions. Strong hydration, i.e., a large quantity of protons, is needed for PEM films to achieve good dissociation and sufficient ionic conductivity. In contrast to PEMs, PILs studied in this work possess small hydrophobic bis(trifluoromethylsulfonyl)imide anions and bulky aprotic cations. There are several possible explanations for water influence on the conductivity of PILs. First, water can plasticize the polymer.[42] Second, water can increase the polarity. And finally, water can increase the dissociation of the counterions and, thus, give the rise to PIL's conductivity. Nevertheless, the mechanism of conduction is believed to be ionic.

■ CONCLUSIONS

Four different ionic monomers, including two novel ones, bearing quaternized imidazolium or pyrrolidinium cations were synthesized and characterized. Their free radical polymerization was studied in detail. Such monomers were found to be suitable for the preparation of high molar mass "polymeric ionic liquids". As previously observed for other families of PILs, their properties such as solubility, viscosity, thermal stability, T_g, and ionic conductivity are affected by the constitution of ILMs. Overall, for the polyanions and polycations synthesized and studied herein can be concluded: Polyanions could be produced with higher molar masses than polycations. Polycations possess lower glass transition temperatures than respective polycations. The bulk ionic conductivity is generally higher for polycations. The ionic conductivity of hydrophilic polyanions strongly depends on the humidity. The thermal stability of the polyanions concedes to that of cationic PILs. Imidazolium-based PILs offer better properties than their pyrrolidinium analogues in terms of ionic conductivity and thermal stability.

The copolymerization of ILMs with **PEGDM** could be an option for the preparation of novel conducting solid polymer electrolytes representing tight, elastic, and free-standing films with good mechanical properties. The possibility to increase the bulk ionic conductivity was found in terpolymerization of oppositely charged ionic monomers with **PEGDM**. Because of the interaction of the pendant ionic substituents and the subsequent ion exchange, the formation of mobile ionic liquid molecules occurred inside the copolymer matrix, which in its turn improves the ion transport.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed ^{1}H NMR spectra of **M3** and **M4**, DSC thermograms for **M1** and **M3**, and reduced viscosity plots for **PIL1** and **PIL3** in various solvents, AUC raw data fits for **PIL1** and **PIL3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Ohno, H.; Ito, K. *Chem. Lett.* **1998**, *27*, 751–752.

(2) Ohno, H.; Yoshizawa, M. Preparation and properties of polymerized ionic liquids as film electrolytes. In *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities: Transformations and Processes*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symp. Ser. Vol. 902; American Chemical Society: Washington, DC, 2005; Chapter 13.

(3) Shaplov, A. S.; Lozinskaya, E. I.; Vygodskii, Y. S. Polymer Ionic Liquids: Synthesis, Design and Application in Electrochemistry as Ion Conducting Materials. In *Electrochemical Properties and Applications of Ionic Liquids*; Torriero, A. A. J., Shiddiky, M. J. A., Eds.; Nova Publishers: New York, 2010; Chapter 9.

(4) Ohno, H. *Macromol. Symp.* **2007**, *249*—*250*, 551–556.

(5) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, 2007.

(6) Appetecchi, G. B.; Kim, G.-T.; Montanino, M.; Carewska, M.; Marcilla, R.; Mecerreyes, D.; De Meatza, I. *J. Power Sources* **2010**, *195*, 3668–3675.

(7) Washiro, S.; Yoshizawa, M.; Nakajima, H.; Ohno, H. *Polymer* **2004**, *45*, 1577–1582.

(8) Ogihara, W.; Washiro, S.; Nakajima, H.; Ohno, H. *Electrochim. Acta* **2006**, *51*, 2614–2619.

(9) Vygodskii, Y. S.; Shaplov, A. S.; Lozinskaya, E. I.; Lyssenko, K. A.; Golovanov, D. G.; Malyshkina, I. A.; Gavrilova, N. D.; Buchmeiser, M. R. *Macromol. Chem. Phys.* **2008**, *209*, 40–51.

(10) Yoshizawa, M.; Ohno, H. *Electrochim. Acta* **2001**, *46*, 1723–1728.

(11) Ohno, H.; Yoshizawa, M.; Ogihara, W. *Electrochim. Acta* **2004**, *50*, 255–261.

(12) Juger, J.; Meyer, F.; Vidal, F.; Chevrot, C.; Teyssié, D. *Tetrahedron Lett.* **2009**, *50*, 128–131.

(13) Vidal, F.; Juger, J.; Chevrot, C.; Teyssié, D. *Polym. Bull.* **2006**, *57*, 473–480.

(14) Chen, H.; Choi, J.-H.; Salas-de la Cruz, D.; Winey, K. I.; Elabd, Y. A. *Macromolecules* **2009**, *42*, 4809–4816.

(15) Borah, P.; Dutta, A. *Ionics* **2008**, *14*, 313–321.

(16) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210*—*211*, 831–835.

(17) Akgöl, Y.; Hofmann, C.; Karatas, Y.; Cramer, C.; Wiemhöfer, H.-D.; Schönhoff, M. *J. Phys. Chem. B* **2007**, *111*, 8532–8539.

(18) Akgöl, Y.; Cramer, C.; Hofmann, C.; Karatas, Y.; Wiemhöfer, H.-D.; Schönhoff, M. *Macromolecules* **2010**, *43*, 7282–7287.

(19) Ogihara, W.; Suzuki, N.; Nakamura, N.; Ohno, H. *Polym. J.* **2006**, *38*, 117–121.

(20) Yoshizawa, M.; Ogihara, W.; Ohno, H. *Polym. Adv. Technol.* **2002**, *13*, 589–594.

(21) Paulechka, Y. U.; Kabo, G. J.; Blokhin, A. V.; Shaplov, A. S.; Lozinskaya, E. I.; Vygodskii, Y. S. *J. Chem. Termodyn.* **2007**, *39*, 158–166.

(22) Shaplov, A. S.; Goujon, L.; Vidal, F.; Lozinskaya, E. I.; Meyer, F.; Malyshkina, I. A.; Chevrot, C.; Teyssié, D.; Odinets, I. L.; Vygodskii, Y. S. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4245–4266.

(23) Vygodskii, Y. S.; Mel'nik, O. A.; Lozinskaya, E. I.; Shaplov, A. S.; Malyshkina, I. A.; Gavrilova, N. D.; Lyssenko, K. A.; Antipin, M. Y.; Golovanov, D. G.; Korlyukov, A. A.; Ignat'ev, N.; Welz-Biermann, U. *Polym. Adv. Technol.* **2007**, *18*, 50–63.

(24) Lewandowski, A.; Swiderska-Mocek, A. *J. Power Sources* **2009**, *194*, 601–609.

(25) Shaplov, A. S.; Lozinskaya, E. I.; Ponkratov, D. O.; Malyshkina, I. A.; Vidal, F.; Aubert, P.-H.; Okatova, O. V.; Pavlov, G. M.; Wandrey, C.; Vygodskii, Y. S. *Electrochim. Acta* **2011** in print (DOI: 10.1016/j.electacta.2011.06.041).

(26) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley and Sons Inc.: Hoboken, NJ, 2004.

(27) Kaim, A. *J. Polym. Sci., Part C: Polym. Lett.* **1984**, *22*, 203–208.

(28) Fuchise, K.; Sone, M.; Miura, Y.; Sakai, R.; Narumi, A.; Sato, S.-I.; Satoh, T.; Kakuchi, T. *Polym. J.* **2010**, *42*, 626–631.

(29) Kubisa, P. *Prog. Polym. Sci.* **2009**, *34*, 1333–1347.

(30) Xie, M.; Han, H.; Ding, L.; Shi, J. *Polym. Rev.* **2009**, *49*, 315.

(31) Strehmel, V. *Macromol. Symp.* **2007**, *254*, 25–33.

(32) Schmidt-Naake, G.; Woecht, I.; Schmalfuß, A. *Macromol. Symp.* **2007**, *259*, 226–235.

(33) Vygodskii, Y. S.; Sapozhnikov, D. A.; Shaplov, A. S.; Lozinskaya, E. I.; Ignat'ev, N. V.; Schulte, M.; Vlasov, P. S.; Malyshkina, I. A. *Polym. J.* **2011**, *43*, 126–135.

(34) Vygodskij, Y. S.; Lozinskaya, E. I.; Shaplov, A. S. *Vysokomol. Soed. (Polym. Sci. J.), Ser. C* **2001**, *43*, 236–251.

(35) Hong, K.; Zhang, H.; Mays, J. W.; Visser, A. E.; Brazel, C. S.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *Chem. Commun.* **2002**, 1368–1369.

(36) Harrisson, S.; Mackenzie, S. R.; Haddleton, D. M. *Macromolecules* **2003**, *36*, 5072–5075.

(37) Chesnokov, S. A.; Zakharina, M. Y.; Shaplov, A. S.; Lozinskaya, E. I.; Malyshkina, I. A.; Abakumov, G. A.; Vidal, F.; Vygodskii, Y. S. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2388–2409.

(38) Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Farrar, D. H.; Lough, A. J.; Loh, W.; da Silva, L. H. M.; Dupont, J. *J. Phys. Chem. B* **2005**, *109*, 4341–4349.

(39) Golovanov, D. G.; Lyssenko, K. A.; Antipin, M. Y.; Vygodskii, Y. S.; Lozinskaya, E. I.; Shaplov, A. S. *Cryst. Growth Des.* **2005**, *5*, 337–340.

(40) Losada, R.; Wandrey, C. *Macromol. Rapid Commun.* **2008**, *29*, 252–257.

(41) Losada, R.; Wandrey, C. *Macromolecules* **2009**, *42*, 3285–3293.

(42) Cramer, C.; De, S.; Schonhoff, M. *Phys. Rev. Lett.* **2011**, *107*, 028301.