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Protic and aprotic anionic oligomeric ionic liquids

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ABSTRACT

We report on synthesis of linear and hyperbranched protic and aprotic anionic oligomeric ionic liquids (OILs). α,ω-Dicarboxy- and α,ω-disulfooligo(ethylene oxide)s, α-carboxy- and α-sulfooligo(ethylene oxide monomethyl ether)s, and di[(α-carboxyoligo(ethylene oxide monomethyl ether)] were synthesized using reaction of oligo(ethylene oxide diol) (MW 1000) and its monomethyl ether (MW 750) with phthalic-, 2-sulfobenzoic anhydride and pyromellitic dianhydride. Di- and mono-substituted anionic OILs were prepared by neutralizing these compounds with N-methylimidazole. Aprotic anionic OILs were synthesized by reaction of sodium salts of the prepared oligomeric di- and monoacids with 1,3-dimethyl imidazolium iodide. Hyperbranched protic and aprotic anionic OILs were prepared in a similar manner. The structure, thermal stability and ionic conductivity of the synthesized compounds in the range of 20–120 °C in anhydrous conditions is governed by the molecular architecture of the oligomeric chains and the type of the cation/anion moieties. OILs under study are amorphous at room temperature but some protic and aprotic linear-chain OILs prone to form a low melting temperature crystalline phase. The ionic conductivity of the synthesized OILs can be varied in broad range reaching 10^{-3} S/cm value at temperatures over 100 °C under anhydrous conditions.

1. Introduction

Organic ionic liquids (IL) represent a new class of electrolytes and are attractive both as a fundamental research field and for practical applications. The practical interest to these compounds is due to their inherently high chemical and electrochemical stability, low flammability, low saturated vapor pressure, and high ionic conductivity. Recent developments of the ionic liquids with polymerizable components have enabled synthesis of polymer ionic liquids, which combine the unique properties of low molecular mass ionic liquids with the macromolecular properties of traditional polymers. This has already led to creation of a new class of polymer electrolytes with a number of prospective applications, which have been highlighted in several recent reviews [1–7]. The papers consider design of cationic, anionic and zwitterionic polymeric ionic liquids (PIL) for creation of various functional materials [2,4,5,7]. Particularly, cationic polymers [6] and their sub-class of imidazolyl-containing PILs [3] have been discussed in details. It should be mentioned that the method of synthesis of polymeric ionic liquids through polymerization of monomeric ionic liquid compounds having a carbon–carbon double bound in their structure is the most developed so far [7].

Due to a hydrophobic character of typical counter-ions constituting ionic liquids most of the PILs do not dissolve in water. They are, nevertheless, soluble in polar organic solvents that distinguish them from classic (i.e., water soluble) electrolytes [4]. Such compounds are losing their low melting transition point property and ability to exist in a liquid state over a broad temperature range when polymerized [4,5]. Therefore, they rather should be considered as polymeric analogs of traditional ionic liquids [8]. However, there are polyacrylate anionic ILs which remain in a liquid state within the range from room temperature to 220 °C thus enabling its application as a solvent and reaction medium [9].

Polymer chemistry distinguishes oligomer materials as a special state of macromolecular compounds [10]. Thus, combining

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properties of ionic liquids with those of oligomers would be interesting for both applied and basic science. So far, the oligomeric state (i.e., an intermediate state between low molecular weight and macromolecular state) of the ionic liquids was barely considered in literature; and the term oligomer ionic liquid (OIL) is not generally accepted yet. The OILs can be broadly defined as ion-containing oligomers that exist in a liquid state below 100 °C (in analogy with ordinary ILs), as well as those that can be viewed as oligomeric analogs of ILs regardless of their aggregate state (following classification suggested in Ref. [8]).

In the latter case, the most important characteristic feature (besides the intermediate “oligomeric-type” molecular weight and a specific aggregate state) is an existence of distinctive for ordinary ILs, so-called “ionic liquid groups” [11], “ionic-liquid functionalities” [12], or “imidazolium-type ionic compounds” [13]. Similarly to traditional ILs [14–16], OILs can be classified as protic or aprotic; while in analogy to the polymer ILs [4,5] they can be also divided into anionic or cationic ones.

Currently, information about OILs is rather fragmentary. Based on the chemical architecture of the oligomeric chains, the existing OIL compounds can be further specified as OILs with linear or brunched structure; star-like or brush-like silicon-organic ones, and dendritic OILs. The first group is represented by α-monosubstituted and α,ω-disubstituted oligoesters and oligoethers having carboxylate, sulfonic [1,17–21], or sulfonamide end groups as salts of alkaline metals [17,22–29]. Let us note that on the contrary to the above mentioned water soluble polymer electrolytes, these anionic oligomer electrolytes exist in the liquid state even at room temperature. The existing cationic linear OILs with imidazolium groups are based on alkylene oxides [30–33] or hydrocarbon chains [13,34,35]. Cationic polymerizable OILs with imidazolium and quaternary ammonium groups were synthesized using monomethacrylic esters of oligo(ethylene oxide diol)s and their derivatives [30,36,37].The second group is represented by silicon organic OILs, which contain either ladder-type oligosilsesquioxane chains [38,39] or the central POSS (octahedral oligomeric silsesquioxane) core [40–48]. The third group is represented by cationic OILs based on hyperbranched oligoester or oligoethers containing quaternary derivatives of imidazolium, pyridine [49] and *tert*-aliphatic amines [50]. A special place in this classification belongs to amphiphilic aliphatic oligoesters of dendritic architecture with quaternary methylimidazole, pyridine or aliphatic *tert*-amine ionic groups in a dendrone focal position [12]. Such molecules show self-assembly properties to form supramolecular dendrimer assemblies of a columnar or spherical type [12]. Synthesis of aliphatic dendrimers with quaternary ammonium groups has been also reported [51,52]. With just a few exceptions, the above mentioned OILs possess one common feature of the special chain end location of their ionic groups.

Synthesized compounds are attractive first of all as ion conducting media useful for various electrochemical devices [4,5,8,14–16]. They are prospective for applications as quasi-solid electrolytes in dye sensitized organic solar cells [38,39], photoluminescence materials [52], nano-scale amphiphilic building blocks in bioengineering and materials science [42,43], nanoreactors for stereo-specific chemical synthesis [12], components of optoelectronic devices [44], heterogeneous catalysts [40], complex forming ligands [31], additives for bio-resistive antimicrobial polymer coatings [45] etc.

It is noteworthy that the above consideration is valid only for the aprotic type OILs, while their protic analogs, to the best of our knowledge, have not been studied yet. Therefore, the aim of present work was in synthesis of linear and hyperbranched anionic protic and aprotic OILs and study of their structure and physical properties.

2. Experimental

2.1. Materials

N-methylimidazole (mim) (Aldrich, 99%), 2-sulfobenzoic acid cyclic anhydride (Aldrich, ≥95%), 3-aminopropyltriethoxysilane (Aldrich, 98%), pyromellitic dianhydride (Aldrich, 97%), were used as received. Phthalic anhydride was purified by sublimation. Oligo(ethylene oxide) monomethyl ether with MW 750 (MePEO-750) and oligo(ethylene oxide)diol with MW 1000 (PEO-1000) (Aldrich) were dried under vacuum conditions using rotary pump (1–3 mm Hg vacuum pressure) at 80–90 °C for 4 h. Hyperbranched aliphatic polyether polyol (HBP) Boltorn®H30 (Perstorp, Sweden) with MW 3500 (an equivalent MW measured by hydroxyl groups via acetylation technique 117 g eq^{-1}) was purified by precipitation of dimethylformamide (DMF) solution in diethyl ether followed by vacuum drying at 25–30 °C for 6 h. DMSO, DMF, diethyl ether, ethanol, and dichloroethane were dried and distilled before usage.

2.2. Synthesis of oligomeric carboxylic and sulfonic acids

2.2.1. Synthesis of α-oligo(ethylene oxide) methyl ether monocarboxylic (**MePEO-COOH**, monosulfonic (**MePEO-SO$_3$H**), di [(α-carboxyoligo(ethylene oxide monomethyl ether) dicarboxylic] (**2MePEO-2COOH**), α,ω-oligo(ethylene oxide) dicarboxylic (**PEO-2COOH**), and disulfonic (**PEO-2SO$_3$H**) acids

2.2.1.1. Synthesis of MePEO-COOH. 6.09 g (8.12 mmol) of MePEO-750 and 1.20 g (8.12 mmol) of phthalic anhydride were put in a round-bottom glass flask with Teflon magnetic stir bar. The reaction was held in a bulk under nitrogen flow at 80 °C for 12 h. The resulting compound was first washed with diethyl ether and then dried under vacuum using rotary pump (1–3 mm Hg vacuum pressure) at 50 °C. The reaction yield was 6.27 g (86%). COOH groups content: 5.01% (calculated 5.05%). IR: ν as C–O–C (1110 cm^{-1}), ν C=O (1727 cm^{-1}), ν C–H bonds of CH_2 and CH_3 groups (2869) cm^{-1}), δ C–H bonds of CH_2 and CH_3 groups (1456 cm^{-1}), ν ar C–H (3072 cm^{-1}), ν ar C–C (1569–1608 cm^{-1}) and ν O–H bonds of COOH groups (3295–3693 cm^{-1}). ^1H NMR (DMSO-d_6): 3.32 ($-O-\boldsymbol{CH_3}$), 3.51 ($-(O\boldsymbol{CH_2CH_2})_nO-$) 3.69 ($-O\boldsymbol{CH_2}CH_2OC(O)-$), 4.32 ($-OCH_2C\boldsymbol{H_2}OC(O)-$), 7.61–7.82 ($Ar-\boldsymbol{H}$) ppm.

This general procedure was used for all the obtained carboxyl- and sulfone-containing linear oligomers.

2.2.1.2. Synthesis of MePEO-SO$_3$H. This oligomer was synthesized by reaction of 6.57 g (8.76 mmol) MePEO-750 with 1.61 g (8.76 mmol) of 2-sulfobenzoic acid cyclic anhydride at 75 °C for 1.5–2 h. Yield: 7.44 g (91%). SO_3H groups: determined 8.48%; calculated 8.67%. IR: ν as C–O–C, ν S=O (1108, 1245 cm^{-1}) ν C=O (1729 cm^{-1}), ν C–H bonds of CH_2 and CH_3 groups (2875 cm^{-1}), δ C–H bonds of CH_2 groups (1458 cm^{-1}), ν ar C–H (3064 cm^{-1}) and ν ar C–C (1564–1602 cm^{-1}) and ν O–H bonds of SO_3H groups (3116–3697 cm^{-1}). ^1H NMR (DMSO-d_6): 3.25 ($-O-\boldsymbol{CH_3}$), 3.52 ($-(O\boldsymbol{CH_2CH_2})_nO-$), 3.78 ($-O\boldsymbol{CH_2}CH_2OC(O)-$), 4.24 ($-OCH_2C\boldsymbol{H_2}OC(O)-$), 7.28–7.74 ($-Ar-\boldsymbol{H}$) ppm.

2.2.1.3. Synthesis of 2MePEO-2COOH. This oligomer was synthesized by reaction of 6.07 g (8.09 mmol) MePEO-750 with 0.87 g (4.01 mmol) pyromellitic dianhydride at 100 °C for 12 h. Yield: 6.11 g (88%). COOH groups: detemined 5.07%; calculated 5.24%. IR: ν as C–O–C (1111 cm^{-1}), ν C=O (1728 cm^{-1}), ν C–H bonds of CH_2 and CH_3 groups (2873) cm^{-1}), δ C–H bonds of CH_2 and CH_3 groups (1459 cm^{-1}), ν ar C–H (3069 cm^{-1}), ν ar C–C (1566–1607 cm^{-1}) and ν O–H bonds of COOH groups (3280–3695 cm^{-1}). ^1H NMR (DMSO-d_6): 3.25 ($-O-\boldsymbol{CH_3}$), 3.52 ($-(O\boldsymbol{CH_2CH_2})_nO-$), 3.70 ($-O\boldsymbol{CH_2}CH_2OC(O)-$), 4.37 ($-CH_2C\boldsymbol{H_2}OC(O)-$), 7.96–8.10 ($Ar-\boldsymbol{H}$) ppm.

2.2.1.4. Synthesis of PEO-2COOH. This oligomer was synthesized by reaction of 5.40 g (5.40 mmol) PEO-1000 with 1.60 g (10.8 mmol) of phthalic anhydride at 80 °C for 12 h. Yield: 6.72 g (92%). COOH groups: determined 6.39%; calculated 6.94%. IR: ν as C–O–C (1112 cm^{-1}), ν C=O (1726 cm^{-1}), ν C–H bonds of CH_2 groups (2873 cm^{-1}), δ C–H bonds of CH_2 groups (1450 cm^{-1}), ν ar C–H (3065) cm^{-1}), ν ar C–C (1579–1643 cm^{-1}) and ν O–H bonds of free COOH groups (3327–3689 cm^{-1}). ^1H NMR (DMSO-d_6): 3.53 ($-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$), 3.71 ($-OC\mathbf{H_2}CH_2OC(O)-$), 4.34 ($-OCH_2C\mathbf{H_2}OC(O)-$), 7.60–7.82 ($Ar-\mathbf{H}$) ppm.

2.2.1.5. Synthesis of PEO-2SO_3H. This oligomer was synthesized by reaction of 4.96 g (4.96 mmol) PEO-1000 with 1.83 g (9.92 mmol) of 2-sulfobenzoic acid cyclic anhydride at 75 °C for 1.5–2.0 h. Yield: 6.07 g (85%). SO_3H groups: determined 11.3%; calculated 11.84%. IR: ν as C–O–C, ν S=O (1099, 1252 cm^{-1}) ν C=O (1734 cm^{-1}), ν C–H bonds of CH_2 and CH_3 groups (2873 cm^{-1}), δ C–H bonds of CH_2 groups (1452 cm^{-1}), ν ar C–H (3070 cm^{-1}) and ν ar C–C (1573–1592 cm^{-1}) and ν O–H bonds of SO_3H groups (3135–3681 cm^{-1}). ^1H NMR (DMSO-d_6): 3.51 ($-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$), 3.69 ($-OC\mathbf{H_2}CH_2OC(O)-$), 4.24 ($-OCH_2C\mathbf{H_2}OC(O)-$), 7.23–7.80 ($-Ar-\mathbf{H}$), 7.74 ($-SO_2-O\mathbf{H}$) ppm.

*2.2.2. Synthesis of hyperbranched oligomeric carboxylic (**HBP-32COOH**) and sulfonic (**HBP-32SO_3H**) acids*

2.2.2.1. Synthesis of HBP-32COOH. This oligomer was synthesized by reaction of 2.04 g (0.0183 g-equivalent) HBP and 2.71 g (0.0183 g-equivalent) of phthalic anhydride in 12 ml DMF at 80 °C for 10–12 h. Yield: 4.02 g (85%). COOH groups: determined 17.33%; calculated 16.05%. IR: ν as C–O–C, (1122, 1255 cm^{-1}) ν C=O (1728 cm^{-1}), ν C–H bonds of CH_2 groups (2931 cm^{-1}), δ C–H bonds of CH_2 groups (1466 cm^{-1}), ν ar C–C (1519–1645 cm^{-1}) and ν O–H bonds of COOH groups (3237–3713 cm^{-1}). ^1H NMR (DMSO-d_6): 1.07–1.21 ($C\mathbf{H_3}-$), 3.44 ($-OC\mathbf{H_2}C\mathbf{H_2}OC(O)-$), 4.17–4.34 ($-C(CH_3)(COO-)C\mathbf{H_2}OC(O)-$, $-OC\mathbf{H_2}C(C\mathbf{H_2}O-)_3-$), 7.25–8.17 ($-Ar-\mathbf{H}$) ppm.

2.2.2.2. Synthesis of HBP-32SO_3H. This oligomer was synthesized by reaction of 1.51 g (0.0135 g-equivalent) HBP and 2.49 g (0.0135 g-equivalent) of 2-sulfobenzoic acid cyclic anhydride in 7 ml DMF at 80 °C for 8–10 h. Yield: 3.87 g (97%). SO_3H groups: determined 25.1%; calculated 26.8%. IR: ν S=O (1018, 1076 cm^{-1}) ν C=O (1726 cm^{-1}), ν C-H bonds of CH_2 groups (2870 cm^{-1}), δ C–H bonds of CH_2 groups (1450 cm^{-1}), ν ar C–C (1495–1636 cm^{-1}). ^1H NMR (DMSO-d_6): 1.08–1.21 ($C\mathbf{H_3}-$), 3.68 ($-OC\mathbf{H_2}C\mathbf{H_2}OC(O)-$), 4.13–4.34 ($-C(CH_3)(COO-)C\mathbf{H_2}OC(O)-$, $-OC\mathbf{H_2}C(C\mathbf{H_2}O-)_3-$), 7.28–8.43 ($-Ar-\mathbf{H}$), 7.75 ($-SO_2-O\mathbf{H}$) ppm.

2.3. Synthesis of oligomeric ionic liquids (OLIs)

2.3.1. Synthesis of protic oligomeric ionic liquids

2.3.1.1. Synthesis of $[MePEO\text{-}COO]^-[Hmim]^+$. A solution of 4.81 g (5.35 mmol) of MePEO-COOH and 0.66 g (8.03 mmol) of 1-methylimidazole in 8 ml of ethanol was intensively stirred at room temperature for 5–10 min. The solvent was then evaporated under low pressure and the obtained viscous transparent yellowish liquid was washed with diethyl ether and dried in vacuum using rotary pump (1–3 mm Hg vacuum pressure) at 40-50°C. Yield: 5.31 g (97%). IR: ν as C–O–C (1106 cm^{-1}), ν C=O (1727 cm^{-1}), ν C–H bonds of CH_2 and CH_3 groups (1871 cm^{-1}), δ C–H bonds of CH_2 and CH_3 groups (1450 cm^{-1}), ν ar C–H (3076 cm^{-1}), ν ar C–C (1506–1618 cm^{-1}), ν C–H bonds of immidazolium cation (3139 cm^{-1}), ν comb N^+-H (3290–3700 cm^{-1}). ^1H NMR (DMSO-d_6): 3.25 ($-O-C\mathbf{H_3}$), 3.52 ($-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$), 3.70 ($-OC\mathbf{H_2}CH_2OC(O)-$), 4,32 ($-OCH_2C\mathbf{H_2}OC(O)-$), 3.67 ($-N(C\mathbf{H_3})-$), 6.94 ($-NH^+-CH=\mathbf{CH}-N-$), 7.15 ($-NH^+-\mathbf{CH}=CH-N-$), 7.64–8.24 ($-NH^+=\mathbf{CH}-N-$, $Ar-\mathbf{H}$) ppm.

This general procedure was used for all the obtained carboxyl- and sulfone-containing protic oligomeric ionic liquids.

2.3.1.2. Synthesis of $[MePEO\text{-}SO_3]^-[Hmim]^+$. 6.48 g (6.94 mmol) MePEO-SO_3H, 0.86 g (10.41 mmol) mim. Transparent viscous liquid of brownish color. Yield: 7.05 g (96%). IR: ν as C–O–C, ν S=O (1105, 1251 cm^{-1}) ν C=O (1726 cm^{-1}), ν C–H bonds of CH_2 and CH_3 groups (2873 cm^{-1}), δ C–H bonds of CH_2 groups (1457 cm^{-1}), ν ar C–H (3072 cm^{-1}), ν ar C–C (1538–1606 cm^{-1}), ν C–H bonds of immidazolium cation (3143 cm^{-1}), ν comb N^+-H (3309–3706 cm^{-1}). ^1H NMR (DMSO-d_6): 3.25 ($-O-C\mathbf{H_3}$), 3.52 ($-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$), 3.73 ($-OC\mathbf{H_2}CH_2OC(O)-$), 4.26 ($-OC\mathbf{H_2}CH_2OC(O)-$), 3.82 ($-N(C\mathbf{H_3})-$), 7.20–7.76 ($-NH^+-CH=\mathbf{CH}-N-$, $-NH^+-\mathbf{CH}=CH-N-$, $-NH^+=\mathbf{CH}-N-$, $Ar-\mathbf{H}$) ppm.

2.3.1.3. Synthesis of $[2MePEO\text{-}2COO]^{2-}2[Hmim]^+$. 4.68 g (2.73 mmol) 2MePEO-2COOH, 0.56 g (6.81 mmol) mim, White color viscous liquid with a yellowish tint which could be extracted from a solution. Yield: 4.93 g (94%). IR: ν as C–O–C (1105 cm^{-1}), ν C=O (1729 cm^{-1}), ν C–H bonds of CH_2 and CH_3 groups (2871 cm^{-1}), δ C–H bonds of CH_2 and CH_3 groups (1454 cm^{-1}), ν ar C–H (3072 cm^{-1}), ν ar C–C (1537–1614 cm^{-1}), ν C–H bonds of immidazolium cation (3145 cm^{-1}), ν comb N^+-H (3178–3689 cm^{-1}). ^1H NMR (DMSO-d_6): 3.25 ($-O-C\mathbf{H_3}$), 3.52 ($-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$), 3.70 (($-OC\mathbf{H_2}CH_2OC(O)-$), 4.37 (($-OCH_2C\mathbf{H_2}OC(O)-$), 3.70 ($-N(C\mathbf{H_3})-$), 7.17 ($-NH^+-CH=\mathbf{CH}-N-$), 7.33 ($-NH^+-\mathbf{CH}=CH-N-$), 7.96–8.10 ($-NH^+=\mathbf{CH}-N-$, $Ar-\mathbf{H}$) ppm.

2.3.1.4. Synthesis of $[PEO\text{-}2COO]^{2}-^{2[Hmim]+}$. 2.66 g (2.05 mmol) PEO-2COOH, 0.34 g (4.11 mmol) mim, Transparent viscous liquid with brownish tint which could be extracted from a solution. Yield: 2.82 g (94%). IR: ν as C–O–C (1112 cm^{-1}), ν C=O (1716 cm^{-1}), ν C–H bonds of CH_2 groups (2875 cm^{-1}), δ C–H bonds of CH_2 (1473 cm^{-1}), ν ar C–H (3076 cm^{-1}), ν ar C–C (1537–1667 cm^{-1}), ν C–H bonds of imidazolium cation (3130 cm^{-1}), ν comb N^+-H (3198–3693 cm^{-1}). ^1H NMR (DMSO-d_6): 3.52 ($-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$ (a)), 3.67 ($-OC\mathbf{H_2}CH_2OC(O)-$ (b)), 3.71 ($-N(C\mathbf{H_3})-$ (i)), 4.33 ($-CH_2C\mathbf{H_2}OC(O)-$ (c)), 6.96 ($-NH^+-CH=\mathbf{CH}-N(CH_3)-$ (j)), 7.16 (($-NH^+-\mathbf{CH}=CH-N(CH_3)-$ (k)), 7.65–7.77 ($Ar-\mathbf{H}$, $-NH^+=\mathbf{CH}-N(CH_3)-$ (d – h)) ppm.

2.3.1.5. Synthesis of $[PEO\text{-}2SO_3]^{2-}2[Hmim]^+$. 2.679 g (1.96 mmol) PEO-2SO_3H, 0.32 g (3.92 mmol) mim. Transparent brownish viscous liquid which could be extracted from a solution. Yield: 2.43 g (81%). IR: ν as C–O–C, ν S=O (1109, 1250 cm^{-1}), ν C=O (1728 cm^{-1}), ν C–H bonds of CH_2 (2883 cm^{-1}) groups, δ C–H bonds of CH_2 groups (1463 cm^{-1}), ν ar C–H (3074 cm^{-1}), ν ar C–C (1558–1641 cm^{-1}), ν C–H bonds of imidazolium cation (3145 cm^{-1}), ν comb N^+-H (3342–3690 cm^{-1}). ^1H NMR (DMSO-d_6): 3.51 ($-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$), 3.70 ($-OC\mathbf{H_2}CH_2OC(O)-$), 3.87 ($-N(C\mathbf{H_3})-$), 4.23 ($-OCH_2C\mathbf{H_2}OC(O)-$), 7.28–7.75 ($-N(CH_3)^+-\mathbf{CH}=\mathbf{CH}-N(CH_3)-$, $Ar-\mathbf{H}$), 9.02 ($-N(CH_3)^+=\mathbf{CH}-N(CH_3)-$) ppm.

2.3.1.6. Synthesis of $[HBP\text{-}32COO]^{32-}32[Hmim]^+$. 1.679 g (7.18 mg-equivalent) HBO-32COOH, 0.88 g (10.76 mg-equivalent) mim. Transparent brownish viscous liquid which could be extracted from a solution. Yield: 2.06 g (91%). IR: ν as C–O–C, (1078, 1126 cm^{-1}) ν C=O (1730 cm^{-1}), ν C–H bonds of CH_2 groups (2960 cm^{-1}), δ C–H bonds of CH_2 groups (1473 cm^{-1}), ν ar C–C (1567–1591 cm^{-1}), ν C–H bonds of imidazolium cation (3151 cm^{-1}), ν comb N^+-H (3200–3703 cm^{-1}). ^1H NMR (DMSO-d_6): 1.05–1.26 ($C\mathbf{H_3}-$ (a)), 3.44 ($-OC\mathbf{H_2}C\mathbf{H_2}OC(O)-$ (c)), 3.66 ($-N(C\mathbf{H_3})-$ (l)), 3.99 ($-C(CH_3)(COO-)C\mathbf{H_2}C_2OC(O)-$ (b)), 4.25 ($-OC\mathbf{H_2}C(C\mathbf{H_2}O-)_3$ (d)), 6.98 ($-N(CH_3)^+-$

$CH{=}\boldsymbol{CH}{-}N(CH_3){-}$ (j)), 7.18 ($-N(CH_3)^+{-}\boldsymbol{CH}{=}CH{-}N(CH_3){-}$ (i)), 7.55–8.15 ($-Ar{-}\boldsymbol{H}$ (e–h), $-NH^+{=}\boldsymbol{CH}{-}N(CH_3){-}$ (k)) ppm.

2.3.1.7. Synthesis of $[HBP\text{-}32SO_3]^{32-}32[Hmim]^+$. 3.40 g (10.53 mg-equivalent) of HBP-32SO$_3$H and 1.30 (15.80 mg-equivalent) mim were added to 13 ml of DMF and kept at room temperature for 5–10 min. The solvent was then removed under low pressure and the remaining transparent brownish liquid was washed with acetone and dried under 60–70 °C in vacuum using rotary pump (1–3 mm Hg vacuum pressure). Yield: 3.37 g (79%). IR: ν S=O (1020, 1083 cm^{-1}) ν C=O (1729 cm^{-1}), ν C–H bonds of CH$_2$ groups (2853 cm^{-1}), δ C–H bonds of CH$_2$ groups (1470 cm^{-1}), ν ar C–C (1495–1652 cm^{-1}), ν C–H bonds of imidazolium cation (3142 cm^{-1}), ν comb N$^+$–H (3222–3706 cm^{-1}). ^{1}H NMR (DMSO-d$_6$): 1.06–1.29 ($\mathbf{C}\boldsymbol{H}_3-$), 3.68 ($-O\boldsymbol{CH_2}CH_2-$), 3.77 ($-N(C\boldsymbol{H_3})-$), 4.12–4.35 ($-C(CH_3)(COO-)C\boldsymbol{H_2}C_2OC(O)-$, $-OC\boldsymbol{H_2}C(C\boldsymbol{H_2}O-)_3-$), 7.29–8.15 ($-Ar{-}\boldsymbol{H}$, $-NH^+{-}\boldsymbol{CH}{=}\boldsymbol{CH}{-}N(CH_3)-$), 8.47 ($-NH^+{=}\boldsymbol{CH}{-}N(CH_3)-$) ppm.

2.3.2. Synthesis of aprotic OILs

1,3-dimethyl imidazolium iodide (**$[Mmim]^+I^-$**) was synthesized in accordance with [53].

Oligomeric carboxylic and sulfonic acids potassium salts were prepared by the following procedure. MePEO-COOH solution in ethanol (3.84 g or 4.27 mmol per 4 ml of ethanol) was added slowly to 0.24 g (4.27 mmol) solution of KOH in 1 ml of water under intensive stirring. The solvent was evaporated and the remaining compound (MePEO-COOK) was dried in vacuum using rotary pump (1–3 mm Hg vacuum pressure) at 70–80 °C till the constant weight. This general procedure was used for synthesis of other salts: MePEO-SO$_3$K, 2MePEO-2COOK, PEO-2COOK, PEO-2SO$_3$K and HBP-32COOK.

2.3.2.1. Synthesis of $[MePEO\text{-}COO]^-[Mmim]^+$. 0.79 g (3.51 mmol) in 3 ml CH$_2$Cl$_2$ solution of $[Mmim]^+[I]^-$ was added to a 3.29 g (3.51 mmol) solution of MePEO-COOK in 3 ml CH$_2$Cl$_2$n under stirring and left overnight for thorough mixing. The solvent was removed under low pressure and remaining brownish viscous liquid was dissolved in water and extracted with chloroform followed by its evaporation and drying of the remaining product in vacuum using rotary pump (1–3 mm Hg vacuum pressure) at 65–70 °C. Yield: 1.61 g (46%). IR: ν as C–O–C (1101 cm^{-1}), ν C=O (1722 cm^{-1}), ν C–H bonds of CH$_2$ and CH$_3$ groups (1875 cm^{-1}), δ C–H bonds of CH$_2$ and CH$_3$ groups (1456 cm^{-1}), ν ar C–H (3108 cm^{-1}), ν ar C–C (1535–1625 cm^{-1}), ν C–H bonds of imidazolium cation (3158 cm^{-1}). ^{1}H NMR (DMSO-d$_6$): 3.22 ($-O{-}C\boldsymbol{H_3}$), 3.50 ($-(OC\boldsymbol{H_2}C\boldsymbol{H_2})_nO-$), 3.66 ($-OC\boldsymbol{H_2}CH_2OC(O)-$), 4.26 ($-OCH_2C\boldsymbol{H_2}OC(O)-$), 3.84 ($-N(C\boldsymbol{H_3})-$), 9.06 ($-N(CH_3)^+{=}\boldsymbol{CH}{-}N(CH_3)-$), 7.36–8.17 ($-N(CH_3)^+{-}CH{=}\boldsymbol{CH}{-}N(CH_3)-$, $-N(CH_3)^+{-}\boldsymbol{CH}{=}CH{-}N(CH_3)-$, $Ar{-}\boldsymbol{H}$) ppm.

This procedure was also used for the synthesis of $[PEO\text{-}2COO]^2-^{2[Mmim]+}$, $[PEO\text{-}2SO_3]^2-^{2[Mmim]+}$, $[HBP\text{-}32COO]^{32-}32[Mmim]^+$.

2.3.2.2. Synthesis of $[MePEO\text{-}SO_3]^-[Mmim]^+$. 3.69 g (3.79 mmol) PEO-SO$_3$K, 0.85 g (3.79 mmol) $[Mmim]^+[I]^-$, viscous liquid. Yield: 2.15 g (55%). IR: ν as C–O–C, ν S=O (1103, 1240 cm^{-1}), ν C=O (1729 cm^{-1}), ν C–H bonds of CH$_2$ and CH$_3$ groups (2875 cm^{-1}), δ C–H bonds of CH$_2$ groups (1454 cm^{-1}), ν ar C–H (3110 cm^{-1}), ν ar C–C (1552–1605 cm^{-1}), ν C–H bonds of imidazolium cation (3157 cm^{-1}). ^{1}H NMR (DMSO-d$_6$): 3.23 ($-O{-}C\boldsymbol{H_3}$), 3.50 ($-(OC\boldsymbol{H_2}C\boldsymbol{H_2})_nO-$), 3.68 ($-OC\boldsymbol{H_2}CH_2OC(O)-$), 4.27 ($-OC\boldsymbol{H_2}CH_2OC(O)-$), 3.83 ($-N(C\boldsymbol{H_3})-$), 9.02 ($-NH^+{=}\boldsymbol{CH}{-}N-$), 7.24–7.80 ($-N(CH_3)^+{-}CH{=}\boldsymbol{CH}{-}N(CH_3)-$, $-N(CH_3)^+{-}\boldsymbol{CH}{=}CH{-}N(CH_3)-$, $-N(CH_3)^+{=}\boldsymbol{CH}{-}N(CH_3)-$, $Ar{-}\boldsymbol{H}$) ppm.

2.3.2.3. Synthesis of $[2MePEO\text{-}2COO]^{2-}2[Mmim]^+$. A mixture of 3.42 g (1.90 mmol) 2MePEO-2COOK and 0.85 g (3.80 mmol) $[Mmim]^+[I]^-$ in 6 ml of DMSO was kept at room temperature overnight. KI precipitated from OIL in a form of finely dispersed powder; it was removed through a repetitive filtration. After each filtration step the solvent was evaporated from the liquid passed through the filter under low pressure and in case if KI precipitation was still observed the whole procedure was repeated. Such filtration/evaporation cycles were repeated several times until no iodine ions were detected in the liquid with addition of AgNO$_3$ water solution. The solvent was then finally removed from the IL by its evaporation in vacuum using rotary pump (1–3 mm Hg vacuum pressure) at 65–70 °C. Yield: 2.98 g (82%). IR: ν as C–O–C (1105 cm^{-1}), ν C=O (1726 cm^{-1}), ν C–H bonds of CH$_2$ and CH$_3$ groups (1875 cm^{-1}), δ C–H bonds of CH$_2$ and CH$_3$ groups (1459 cm^{-1}), ν ar C–H (3112 cm^{-1}), ν ar C–C (1535–1633 cm^{-1}), ν C–H bonds of imidazolium cation (3160 cm^{-1}). ^{1}H NMR (DMSO-d$_6$): 3.22 ($-O{-}C\boldsymbol{H_3}$), 3.50 ($-(OC\boldsymbol{H_2}C\boldsymbol{H_2})_nO-$), 3.85 ($-OC\boldsymbol{H_2}CH_2OC(O)-$), 4.25 ($-OCH_2C\boldsymbol{H_2}OC(O)-$), 3.85 ($-N(C\boldsymbol{H_3})-$), 9.05 ($-NH^+{=}\boldsymbol{CH}{-}N-$), 7.6–8.19 ($-N(CH_3)^+{-}CH{=}\boldsymbol{CH}{-}N(CH_3)-$, $-N(CH_3)^+{-}\boldsymbol{CH}{=}CH{-}N(CH_3)-$, $Ar{-}\boldsymbol{H}$) ppm.

2.3.2.4. Synthesis of $[PEO\text{-}2COO]^2-^{2[Mmim]+}$. 2.50 g (1.73 mmol) PEO-COOK, 0.78 g (3.46 mmol) $[Mmim]^+[I]^-$, transparent viscous liquid. Yield: 2.30 g (85%). IR: ν as C–O–C (1103 cm^{-1}), ν C=O (1724 cm^{-1}), ν C–H bonds of CH$_2$ groups (2867 cm^{-1}), δ C–H bonds of CH$_2$ (1470 cm^{-1}), ν ar C–H (3083 cm^{-1}), ν ar C–C (1571–1635 cm^{-1}), ν C–H bonds of imidazolium cation (3153 cm^{-1}), ν comb N$^+$–H (3210–3687 cm^{-1}). ^{1}H NMR (DMSO-d$_6$): 3.51 ($-(OC\boldsymbol{H_2}C\boldsymbol{H_2})_nO-$), 3.67 ($-OC\boldsymbol{H_2}CH_2OC(O)-$), 3.85 ($-N(C\boldsymbol{H_3})-$), 4.33 ($-OCH_2C\boldsymbol{H_2}OC(O)-$), 7.49–7.83 ($-N(CH_3)^+{-}\boldsymbol{CH}{=}\boldsymbol{CH}{-}N(CH_3)-$, $Ar{-}\boldsymbol{H}$), 8.16 ($-N(CH_3)^+{=}\boldsymbol{CH}{-}N(CH_3)-$) ppm.

2.3.2.5. Synthesis of $[PEO\text{-}2SO_3]^2-^{2[Mmim]+}$. 3.38 g (2.23 mmol) PEO-SO$_3$K, 1.00 g (4.46 mmol) $[Mmim]^+[I]^-$, transparent viscous liquid. Yield: 2.73 g (75%). IR: ν as C–O–C, ν S=O (1078, 1201 cm^{-1}), ν C=O (1721 cm^{-1}), ν C–H bonds of CH$_2$ (2868 cm^{-1}) groups, δ C–H bonds of CH$_2$ groups (1448 cm^{-1}), ν ar C–H (3093 cm^{-1}), ν ar C–C (1571–1635 cm^{-1}), ν C–H bonds of imidazolium cation (3163 cm^{-1}), ν comb N$^+$–H (3293–3688 cm^{-1}). ^{1}H NMR (DMSO-d$_6$): 3.61 ($-(OC\boldsymbol{H_2}C\boldsymbol{H_2})_nO-$), 3,82 ($-OC\boldsymbol{H_2}CH_2OC(O)-$), 3.96 ($-N(C\boldsymbol{H_3})-$), 4.51 (($-OCH_2C\boldsymbol{H_2}OC(O)-$), 7.24–7.39 ($-N(CH_3)^+{-}\boldsymbol{CH}{=}\boldsymbol{CH}{-}N(CH_3)-$, $Ar{-}\boldsymbol{H}$), 8.10 ($-N(CH_3)^+{=}\boldsymbol{CH}{-}N(CH_3)-$) ppm.

2.3.2.6. Synthesis of $[HBP\text{-}32COO]^{32-}32[Mmim]^+$. 1.93 g (7.10 mg-equivalent) HBP-32COOK, 1.89 g (7.10 mg-equivalent) $[Mmim]^+[I]^-$. The final product was washed with acetone. Ttransparent viscous liquid. Yield: 2.30 g (87%). IR: ν as C–O–C, (1078, 1122 cm^{-1}) ν C=O (1730 cm^{-1}), ν C–H bonds of CH$_2$ groups (2966 cm^{-1}), δ C–H bonds of CH$_2$ groups (1462 cm^{-1}), ν ar C–C (1570–1606 cm^{-1}), ν C–H bonds of imidazolium cation (3064–3157 cm^{-1}). ^{1}H NMR (DMSO-d$_6$): 0.93–1.22 ($\mathbf{C}\boldsymbol{H}_3-$), 3.82 ($-N(C\boldsymbol{H_3})-$), 4.01–4.35 ($-C(CH_3)(COO-)C\boldsymbol{H_2}C_2OC(O)-$, $-OC\boldsymbol{H_2}C(C\boldsymbol{H_2}O-)_3-$), 7.29–8.16 ($-Ar{-}\boldsymbol{H}$, $-N(CH_3)^+{-}\boldsymbol{CH}{=}\boldsymbol{CH}{-}N(CH_3)-$), 9.12 ($-N(CH_3)^+{=}\boldsymbol{CH}{-}N(CH_3)-$) ppm.

The completeness of iodine ion removing procedure from synthesized aprotic OILs was determined via a set of qualitative reactions. Thus, addition of a water solution of AgNO$_3$ (which is a known reactant for iodine ions) and Beilstein's test were applied. In both cases the absence of the iodine ions has been confirmed.

2.4. Instrumentation

Fourier transform infra red (FT-IR) spectra of synthesized compounds were recorded with a TENSOR 37 spectrophotometer

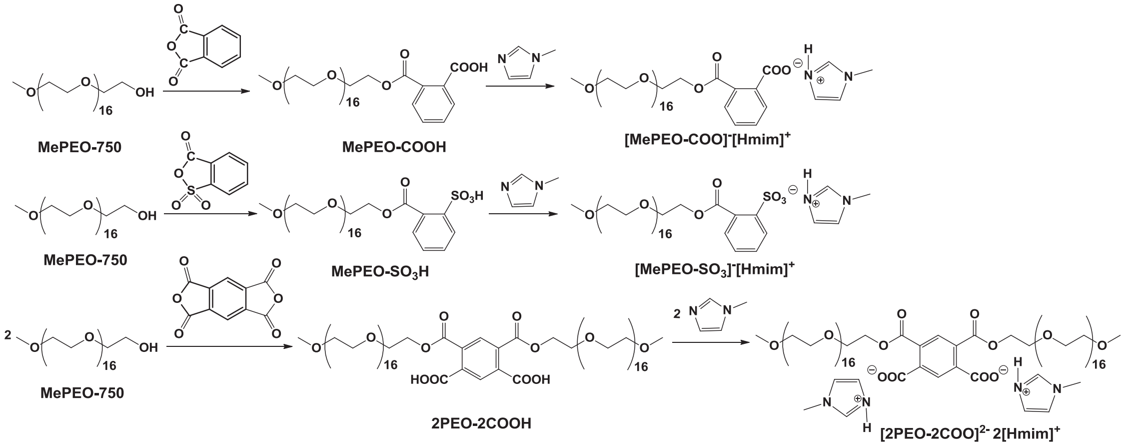

Fig. 1. Synthesis of linear chain α-monosubstituted protic anionic carboxylate and sulfonate OIL.

operated in 600–4000 cm^{-1} range. ^{1}H NMR spectra were recorded with a Varian VXR-400 MHz spectrometer using DMSO-d$_6$ solvent. Thermal characteristics were studied with a Q2000 (TA Instruments, USA) equipment in temperature range 90–200 °C in air with a typical heating rate of 20 °C/min. Thermal mass loss and the starting point of the thermal oxidative degradation (T_d) were determined using a Q50 (TA Instruments, USA) gravimeter via thermal scanning in the range of 20 to 700 °C with the rate of 20 °C/min in air. DC ionic conductivity (σ_{dc}) of the synthesized OILs was measured by the dielectric relaxation spectroscopy technique using a home-made dielectric spectrometer based on a P5083 AC bridge scheme (0.1–100 kHz) and a two-electrode stainless steel cell. Samples were dried for 30 min at 100 °C under nitrogen flow before measurements. The measurements were performed in the nitrogen flow atmosphere in the temperature range of 20–120 °C. The acidic group content in synthesized oligomeric acids was determined by a direct acid–base titration procedure.

3. Results and discussion

Synthesis of anionic protic and aprotic OILs was based on introduction of carboxyl or sulfonic end groups into oligomer chains of various structures followed by their neutralization with N-methylamidozole (mim) (in case of protic OILs) or usage sodium salts of these oligomeric acids in reaction with mim (in case of aprotic OILs). Introduction of carboxylic or sulfonic groups was accomplished through reaction of hydroxyl-modified oligomers of different types and functionality with various acid anhydrides (particularly, phthalic, 2-sulfobenzoic acids and pyromellitic ones). Linear chain oligomers oligo(ethylene oxide)diol with MW 1000 (PEO-1000) and its monomethyl ether with MW 750 (MePEO-750) as well as a third generation hyperbranched poly(ester polyol) (HBP) were used as the initial hydroxylated oligomers for the OILs synthesis. Described synthetic routes for OILs are based on well-known reactions of acylation, metathesis and neutralization with application of commercially available initial compounds; they use relatively simple protocols and characterized as a rule by high yield of the final products.

Thus, α-monosubstituted protic OIL of linear structure [MePEO-COO]$^-$[Hmim]$^+$ and [MePEO-SO$_3$]$^-$[Hmim]$^+$ were synthesized using MePEO-750 and anhydride of phthalic or 2-sulfobenzoic acids as the initial compounds (Fig. 1). Similarly, linear protic OIL of a "butterfly type" [2MePEO-2COO]$^{2-}$2[Hmim]$^+$ was obtained by reaction of MePEO-750 with pyromellitic dianhydride (Fig. 1).

Synthesis of α-monosubstituted MePEO and α,ω-disubstituted PEO with the end carboxylic and sulfonic groups by reaction of MePEO and PEO with acid anhydrides was described earlier [1,21,54,55]. We performed the same reaction in a solvent free environment. Protic α,ω-disubstituted linear carboxylate ([PEO-2SO$_3$]$^{2-}$2[Hmim]$^+$) and sulfonate ([PEO-2SO$_3$]$^{2-}$2[Hmim]$^+$) OILs were synthesized by reaction of PEO-1000 with anhydride of phthalic or 2-sulfobenzoic acids (Fig. 2).

Similar synthetic routes were used for preparation of protic hyperbranched carboxylate [HBP-32COO]$^{32-}$32[Hmim]$^+$ and sulfonate [HBP-32SO$_3$]$^{32-}$32[Hmim]$^+$ OIL (Fig. 3).

Synthesis of aprotic OILs of α-monosubstituted linear chain type ([MePEO-COO]$^-$[Mmim]$^+$, [MePEO-SO$_3$]$^-$[Mmim]$^+$, [MePEO-SO$_3$]$^-$[Mmim]$^+$); α,ω-disubstituted type ([PEO-2COO]$^{2-}$2[Mmim]$^+$, [PEO-2SO$_3$]$^{2-}$2[Mmim]$^+$), and hyperbranched carboxylate ([HBP-32COO]$^{32-}$32[Mmim]$^+$), and sulfonate ([HBP-32SO$_3$]$^{32-}$32[Mmim]$^+$) type are shown in Figs. 4–6, correspondingly. Our synthetic approach was based on reaction of potassium salts of the above mentioned oligomeric mono- and di-acids whith 1,3-dimethyl imidazolium iodide [Mmim]$^+$I$^-$.

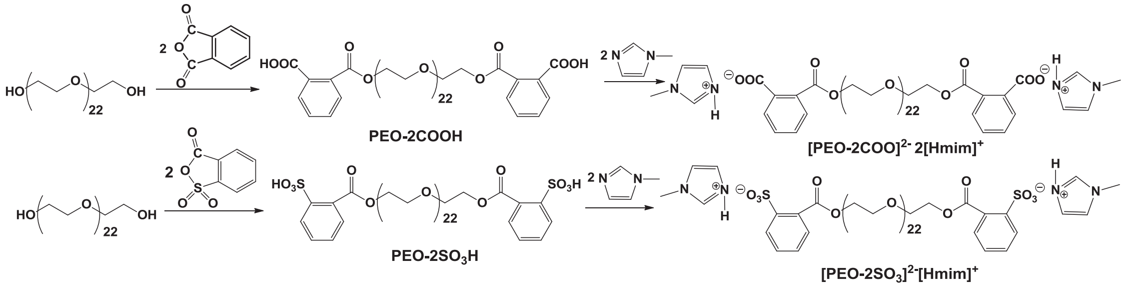

Fig. 2. Synthesis of linear chain α,ω-disubstituted protic anionic carboxylate and sulfonate OIL.

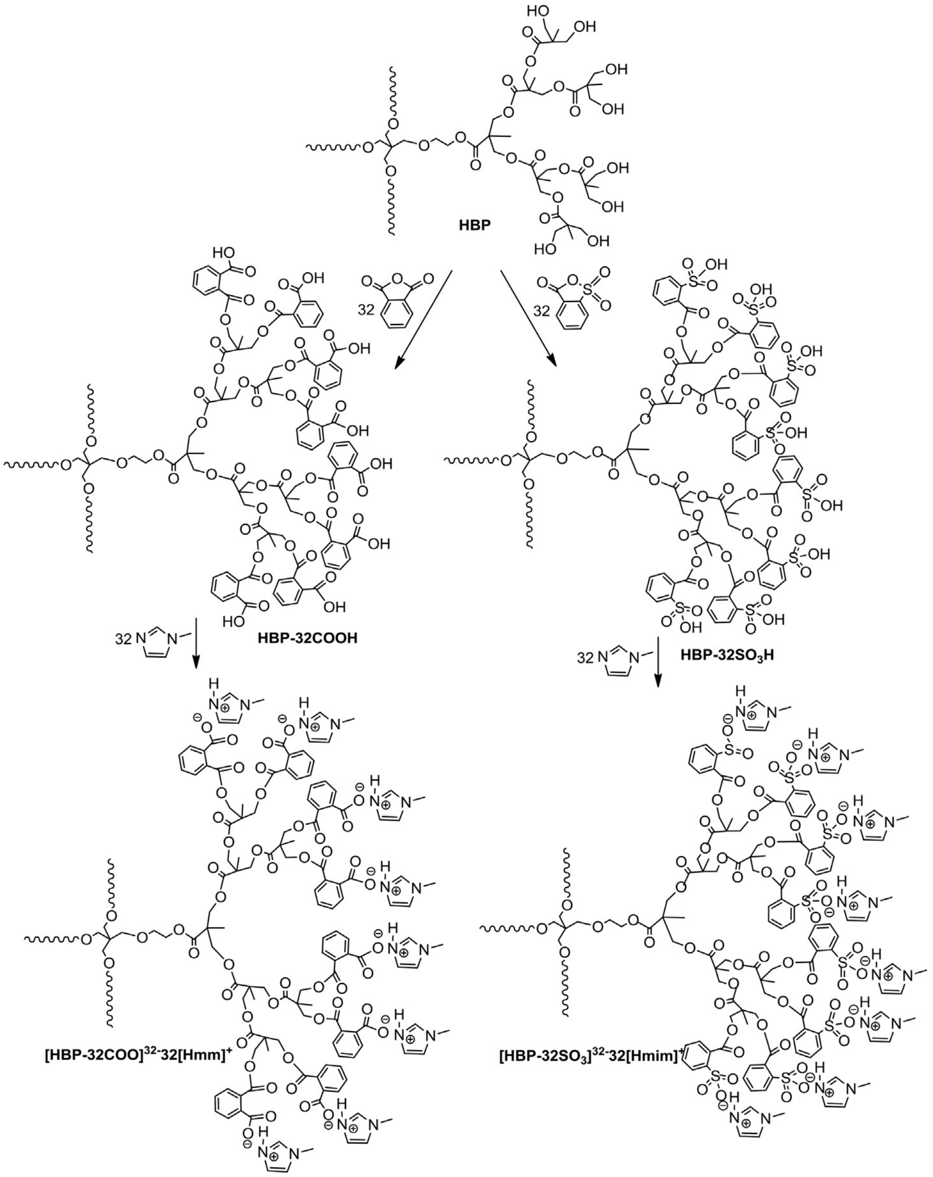

Fig. 3. Synthesis of protic hyperbranched carboxylate and sulfonate OILs.

All synthesized protic and aprotic OILs (both linear and hyperbranched type) behave as sticky viscous liquids at room temperature. They show good solubility in polar solvents such as water, ethanol, DMF, DMSO, and acetonitrile, poor or good solubility in weakly polar or nonpolar solvents such as acetone, ethylacetate, tetrahydrofuran, chloroform, and insolubility in nonpolar solvents such as diethyl ether, hexane, benzene, and toluene. The photographs of one of the synthesized OILs namely [MePEO-COO]$^-$[Hmim]$^+$ (Fig. 7(1)), its 50% solution in acetone (Fig. 7(2)) and phase-separated mixture with hexane (Fig. 7(3)) at room temperature are given at Fig. 7. It can be concluded from the shape of menisci that OIL (Fig. 7(1)) is characterized by a significantly higher viscosity compared to its concentrated solution in acetone (Fig. 7(2)). When OIL mixed with hexane the phase separation of the mixture (Fig. 7(3)) is clearly observed which persists upon heating up to solvent boiling temperature.

Molecular weight of the synthesized OILs determined through end group titration analysis are in a good agreement with the calculated values found through molecular weight of corresponding oligomeric acids and heterocycle (Table 1).

IR spectra of protic and aprotic OILs of a similar structure (i.e., with carboxylic or sulfonic acidic groups) look alike. Fig. 8 shows typical spectra of carboxylic protic OIL of different molecular structure. As can be seen, all the compounds possess vibration bands corresponding to ether and ester fragments. Particularly, stretching modes of C—O—C (ν_{C-O-C} = 1078–1126 cm^{-1}), and C=O ($\nu_{C=O}$ = 1716–1730 cm^{-1}) bonds, as well as vibration modes of aliphatic chains (ν_{C-H} = 2871–2960 cm^{-1}, δ_{C-H} = 1450–1473 cm^{-1}), and aromatic rings (ν_{C-H} = 3072–3151 cm^{-1}, ν_{C-C} = 1506–1667 cm^{-1}) can be clearly identified [56,57]. The IR bands in the range of 3100–3700 cm^{-1} can be assigned either to valent oscillations of imidazoyl cation bonds N$^+$—H or to O—H bonds from sorbed water molecules. Let us note also presence of additional bands corresponding to valent vibrations of S=O groups (1020–1251 cm^{-1}) of sulfonate fragments in sulfonated OILs. Unambigous identification of these groups is problematic due to coincidence of their vibration band position with the valence vibrations of C—O—C ether groups.

^{1}H NMR spectra of similar OILs are also very close. Fig. 9 presents spectra of the discussed above carboxylic protic compounds of

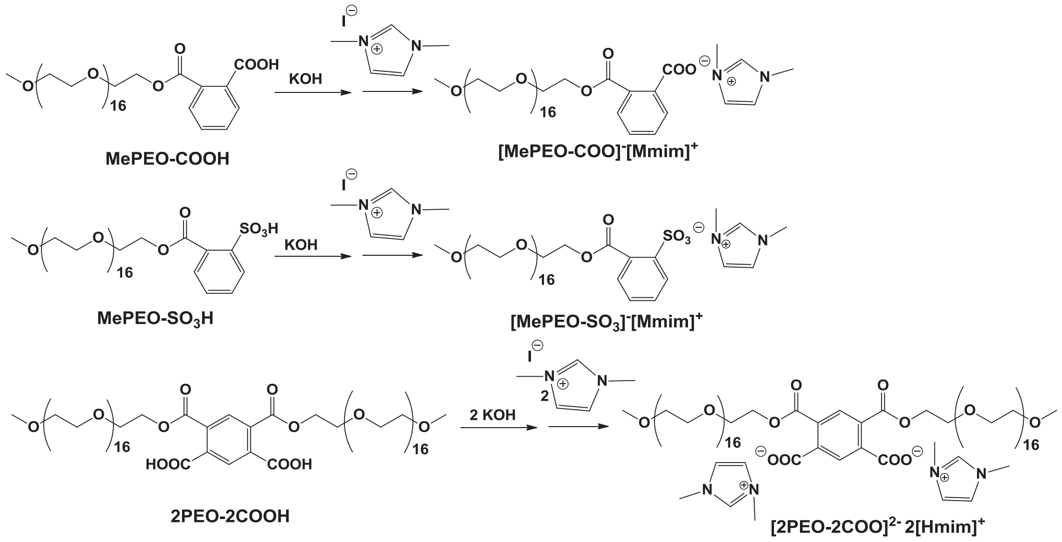

Fig. 4. Synthesis of aprotic OILs of α-monosubstituted linear chain type.

different chemical structure. All the spectra contain peaks corresponding to protons of methylene groups in α substitution relative to the oxygen of an ester fragment: $-OC\mathbf{H_2}CH_2OC(O)-$ (3.44–3.7 ppm), $-OCH_2C\mathbf{H_2}OC(O)-$ (4.32–4.37 ppm). In linear chain compounds (Fig 9., spectra 1, 2, 3) peaks corresponding to protons of ether groups $-(OC\mathbf{H_2}C\mathbf{H_2})_nO-$ (3.52 ppm), methylene groups $-N(C\mathbf{H_3})-$ (3.66–3.71 ppm) and methane groups of imidazoyl cations in 4 and 5 substitution position: $\equiv N^+-\mathbf{CH}=CH-N=$ (7.15–7.33 ppm), $\equiv N^+-CH=\mathbf{CH}-N=$ (6.94–7.17 ppm), as well as those of the aromatic groups and methane groups of the imidazoyl cations in 2 substitution ($-Ar-\mathbf{H}$, $=NH^+=\mathbf{CH}-N-$ (7.64–8.24 ppm)) can be identified [56,57]. Spectra 1 and 2 of OILs based on MePEO-750 have additional peaks corresponding to protons of the end methyl groups (ether fragments $-OCH_3$: 3.52 ppm). The ^1H NMR spectrum of the hyperbranched $[HBP\text{-}32COO]^{32-}32[Hmim]^+$ compound (Fig 9., spectrum 4) contains characteristic proton peaks corresponding to methyl and methylene groups of the ternary carbon atom: 0.93–1.22 ppm ($-CH_3$) and 4.25 ppm ($-OC\mathbf{H_2}C(C\mathbf{H_2}O-)_3$), correspondingly.

Synthesized anionic linear OILs possess flexible oligo(ethylene oxide) backbone with carboxylate and sulfonate methylamidozolium fragments as protic and aprotic ionic groups. They differ by the type and placement of the ionic groups. Using MePEO-750 units, OILs with one terminal ionic group at the one end of their chains – α-monosubstituted oligo(ethylene oxide)s: $[MePEO\text{-}COO]^-[Hmim]^+$, $[MePEO\text{-}SO_3]^-[Hmim]^+$, $[MePEO\text{-}COO]^-[Mmim]^+$, $[MePEO\text{-}SO_3]^-[Mmim]^+$, or with double protic ionic groups bearing two α-methyloligo(ethylene oxide) chains: MePEO-750 $[2MePEO\text{-}2COO]^{2-}2[Hmim]^+$ and $[2MePEO\text{-}2COO]^{2-}2[Mmim]^+$ have been synthesized. Using PEO-1000, OILs terminated with ionic groups from both ends of their oligomeric backbones (i.e., α,ω-disubstituted oligo(ethylene oxide)s): $[PEO\text{-}2COO]^{2-}2[Hmim]^+$, $[PEO\text{-}2SO_3]^{2-}2[Hmim]^+$, $[PEO\text{-}2COO]^{2-}2[Mmim]^+$, $[PEO\text{-}2SO_3]^{2-}2[Mmim]^+$) were obtained. Particular chemical structure of OILs under study causes different ionic group content in comparison to the original ethylene oxide oligomer. Hyperbranched protic ($[HBP\text{-}32COO]^{32-}32[Hmim]^+$, $[HBP\text{-}32SO_3]^{32-}32[Hmim]^+$ and aprotic $[HBP\text{-}32COO]^{32-}32[Mmim]^+$ OIL have oligoester core with terminal carboxylate and sulfonate groups.

In accordance to DSC results (Fig. 10, Table 1), the synthesized OILs are characterized with a single glass transition (a signature of the oligo(ethylene oxide) component). Both the linear chain architecture of OILs under study and the nature of the ionic group have a critical impact on their structure. Let us note that carboxylate OILs have lower T_g in comparison to the sulfonate ones (Table 1). This corresponds to higher chain mobility of the former class. Increase of the ionic group content in α,ω-disubstituted (both carboxylic and sulfonate type) OILs in comparison to α-monosubstituted ones leads to a predictable raise of their T_g caused by their more rigid molecular structure. The lowest T_g belong to a

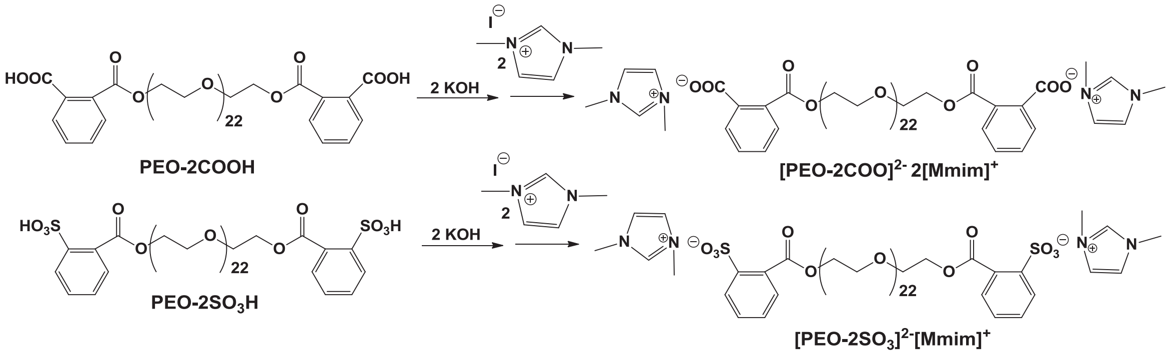

Fig. 5. Synthesis of aprotic OILs of α,ω-disubstituted linear chain type.

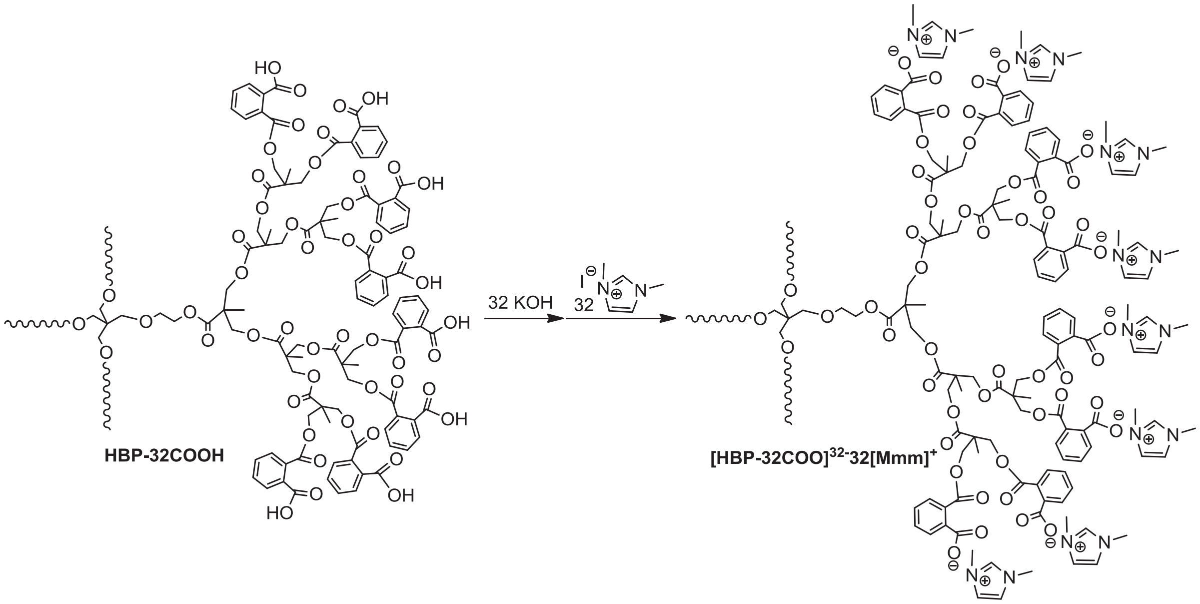

Fig. 6. Synthesis of aprotic hyperbranched anionic carboxylate OIL.

"butterfly type" OILs, which have higher content of a flexible chain component $[2MePEO\text{-}2COO]^{2}{-}^{2[Hmim]+}$.

The typical DSC curves for these compounds are given at Fig. 10. One characteristic feature of all carboxylate protonic OILs: $[MePEO\text{-}COO]^{-}[Hmim]^{+}$, $[2MePEO\text{-}2COO]^{2-}2[Hmim]^{+}$ and $[PEO\text{-}2COO]^{2-}2[Hmim]^{+}$ is an appearance of both exothermic and endothermic peaks in their DSC curves (Fig. 10 curve 2). The former corresponds to a cold crystallization process (T_{cc}) [58], while the latter appears due to a melting process (T_m) giving evidence of a crystalline nature of these compounds. The values of T_{cc} observed for α-monosubstituted carboxylate OILs coincide, and their T_m values are very close (Table 1). An additional shoulder can be observed on the slope of the main T_m peak at 2.9 °C in the DSC curves (in analogy with $[MePEO\text{-}SO_3]^{-}[Hmim]^{+}$ (Fig. 10, curve 1)) of the "butterfly type" OILs ($[2MePEO\text{-}2COO]^{2-}2[Hmim]^{+}$) giving evidence of the presence of crystallites of different morphology in these compounds (Table 1). Presence of carboxylate groups at the both ends (α,ω-disubstituted oligo(ethylene oxide)s) of the chains changes the character of the end-group interaction with the oligoether component. As a result of this, all the characteristic peaks T_{cc}, T_g, and T''_m are observed at higher temperature (Table 1).

Opposite of the above mentioned carboxylate compounds, the cold crystallization peak is not observed in DSC curves of α-monosubstituted sulfonate OILs. Instead, two melting transitions could be revealed with the with the T'_m and T''_m temperatures higher than for $[2MePEO\text{-}2COO]^{2-}2[Hmim]^{+}$ (Table 1). For the α,ω-disubstituted sulfonate OIL compound $[PEO\text{-}2SO_3]^{2-}2[Hmim]^{+}$ only glass transition corresponding to the oligoether component was detected (Fig. 10, curve 3, Table 1).

Protic hyperbranched ester OILs are characterized with much higher T_g value. Such thermodynamic behavior can be attributed to both their more rigid hyperbranched molecular architecture and stronger interaction of their protic ionic groups with ester component of OILs. As a result, the sulfonic OIL compound is also characterized with higher T_g (Table 1).

Aprotic OILs display some peculiarities of their structure and thermal properties in comparison to the protic analogs (Table 1). Linear chain OILs show generally the same trend in their T_g variation depending on the oligomer structure and the type of the ionic groups. Generally, 3–10 °C degrees higher T_g values observed for linear-chain aprotic OILs correspond to stronger interaction between their highly polar ionic groups with the oligoether component. This conclusion is supported by the absence of cold

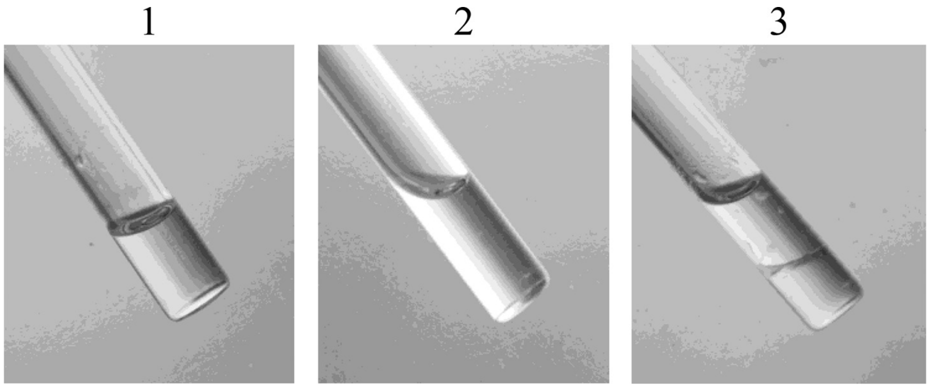

Fig. 7. Photographs of OIL $[MePEO\text{-}COO]^{-}[Hmim]^{+}$ (1), its 50% solution in acetone (2) and the mixture with hexane (3) at room temperature.

Table 1
Characteristics and properties of synthesized protic and aprotic OILs.

Name	MW		T_{cc}, °C	T_m', °C	T_m'', °C	T_g, °C	T_d, °C	σ_{dc}, S/cm			
	Found	Calculated						20 °C	40 °C	100 °C	120 °C
Protic IOL											
$[MePEO\text{-}COO]^{-}[Hmim]^{+}$	980	980	−31.3	–	15.2	−57.7	178	–	$8.24 \cdot 10^{-5}$	$5.40 \cdot 10^{-4}$	$6.99 \cdot 10^{-4}$
$[MePEO\text{-}SO_3]^{-}[Hmim]^{+}$	1037	1016	–	4.3	19.1	−48.2	234	–	$2.00 \cdot 10^{-4}$	$1.72 \cdot 10^{-3}$	$2.44 \cdot 10^{-3}$
$[2MePEO\text{-}2COO]^{2-}2[Hmim]^{+}$	1939	1882	−31.3	2.85	16.5	−73.5	243	–	–	$6.88 \cdot 10^{-4}$	$9.71 \cdot 10^{-4}$
$[PEO\text{-}2COO]^{2-}2[Hmim]^{+}$	1572	1461	−4.4	–	29.0	−46.4	173	–	$7.84 \cdot 10^{-5}$	$7.05 \cdot 10^{-4}$	$9.86 \cdot 10^{-4}$
$[PEO\text{-}2SO_3]^{2-}2[Hmim]^{+}$	1598	1532	–	–	–	−31.4	241	–	$1.27 \cdot 10^{-4}$	$1.54 \cdot 10^{-3}$	$2.33 \cdot 10^{-3}$
$[HBP\text{-}32COO]^{32-}32[Hmim]^{+}$	10,112	10,932	–	–	–	−16.2	145	–	$5.60 \cdot 10^{-6}$	$2.86 \cdot 10^{-4}$	$6.95 \cdot 10^{-4}$
$[HBP\text{-}32SO_3]^{32-}32[Hmim]^{+}$	12,951	12,296	–	–	–	−9.2	270	$6.44 \cdot 10^{-5}$	$4.04 \cdot 10^{-4}$	$3.22 \cdot 10^{-3}$	–
Aprotic OIL											
$[MePEO\text{-}COO]^{-}[Mmim]^{+}$	1037	1037	–	–	–	−53.4	226	–	–	$1.82 \cdot 10^{-3}$	$1.91 \cdot 10^{-3}$
$[MePEO\text{-}SO_3]^{-}[Mmim]^{+}$	1094	1073	–	–	–	−44.7	240	–	–	$1.89 \cdot 10^{-3}$	$2.49 \cdot 10^{-3}$
$[2MePEO\text{-}2COO]^{2-}2[Mmim]^{+}$	2052	1995	−21.0	–	16.1	−62.4	226	–	–	$1.42 \cdot 10^{-3}$	$1.51 \cdot 10^{-3}$
$[PEO\text{-}2COO]^{2-}2[Mmim]^{+}$	1598	1488	–	–	–	−36.8	222	$4.59 \cdot 10^{-5}$	$5.18 \cdot 10^{-4}$	$3.27 \cdot 10^{-3}$	–
$[PEO\text{-}2SO_3]^{2-}2[Mmim]^{+}$	1510	1560	–	–	–	−41.7	259	$3.73 \cdot 10^{-6}$	$6.57 \cdot 10^{-5}$	$7.87 \cdot 10^{-4}$	–
$[HBP\text{-}32COO]^{32-}32[Mmim]^{+}$	11,992	12,734	–	–	–	32.4	185	–	$2.00 \cdot 10^{-10}$	$9.35 \cdot 10^{-8}$	$1.22 \cdot 10^{-6}$

crystallization process in the aprotic OILs under study. The only exception is an aprotic "butterfly type" OILs. However, even for this compound the T_{cc} value is only 10° exceeding the corresponding value of the protic analog. Very close values of melting transitions observed for aprotic and protic "butterfly type" OILs thus justifying the similarity of their crystalline organization (Table 1). Obviously, stronger interaction between aprotic ionic groups and oligoester component together with their hyperbranched architecture lead to a dramatic (almost 50 °C) increase of their glass transition temperature ($[HBP\text{-}32COO]^{32-}32[Mmim]^{+}$ (Table 1).

In accordance to the TGA analysis (Table 1), the degradation temperature, T_d (corresponding to a 5% mass loss), is higher for protic sulfonated linear chain OILs in comparison to the carboxylate analogs. The difference in T_d is as high as 60 °C. OILs with the "butterfly type" structure show unusually high thermal stability. This should be related to a high charge density on their ionic end groups (Table 1). An effect of the ionic groups on the thermal stability is the most obvious when comparing properties of carboxylate and sulfonate type protic hyperbranched OIL. The hyperbranched OIL compound with sulfonate ionic groups has much higher thermal stability (its T_d is 125° higher). Aprotic OIL compounds possess T_d values similar to those of protic ones with higher thermal stability observed for sulfonate-containing oligomers. However, the spread of the corresponding values depending on the molecular structure is not as broad as in protic OILs. Similarly to the case of protic compounds, the worst thermal stability (the smallest T_d value) is observed in aprotic hyperbranched carboxylated OILs (Table 1).

Synthesized OILs are promising for application requiring anhydrous ion-conducting media. As discussed in previous publications, the ionic conductivity of such anhydrous materials is determined by the concentration and mobility of charge carriers [1,17–21]. In the synthesized protic compounds oligoether (linear OIL) or oligoester (hyperbranched OIL) component of OILs are responsible for the appearance of the ion-conductivity. In case of protic OILs ionic conductivity is characterized with a Grotthuss conductivity mechanism related to a segmental mobility of this flexible chain component of the materials [1,17–21].

As follows from Fig. 11 and Table 1, the ionic conductivity (σ_{dc}) of the synthesized protic and aprotic OILs is increasing with temperature, which is a characteristic feature of the ionic conductivity [59]. Within the synthesized row the conductivity is higher for the case when stronger sulfonic acid is used as a neutralizing agent. The maximal conductivity value of $2.44 \cdot 10^{-3}$ S/cm at 120 °C belongs to the linear chain α-monosubstituted compound (Table 1). For carboxyl type protic OIL the structure of the oligomer component has a small influence on the σ_{dc} value. In this case no correlation between σ_{dc} and T_g values could be found. Moreover, in case of hyperbranched architecture of the protic OIL (both carboxylic and sulfonic type) higher ionic conductivity is observed due to higher proton concentration at higher glass transition temperature. This is especially true for sulfonic type OIL where the ionic conductivity reaches $2.33 \cdot 10^{-3}$ S/cm at 120 °C ($T_g = -9.2$ °C) (see Table 1).

Close consideration of the aprotic monosubstituted OILs reveals that the nature of the counter ion does not play so important role for their conductivity properties. Their σ_{dc} values are of the order of $\sim 10^{-3}$ S/cm in the range of 100–120 °C, with just slightly higher value for the sulfonated compound (Table 1). Similarly to protic OILs, there is no direct correlation between the conductivity and glass transition values in this case. However, lower σ_{dc} values for aprotic α,ω-disubstituted sulfonated OILs $[PEO\text{-}2SO_3]^{2-}2[Mmim]^{+}$ as well as the above mentioned low T_g (−41.7 °C) for these compounds are quite unexpected (Table 1).

When linear chains are substituted with hyperbranched ones in an aprotic OIL (i.e., the molecular structure is changed considerably due to introducing an oligoester component), both a sharp increase of the glass transition and dramatic (3–4 orders of the magnitude) decrease of the ionic conductivity in comparison to the linear-chain

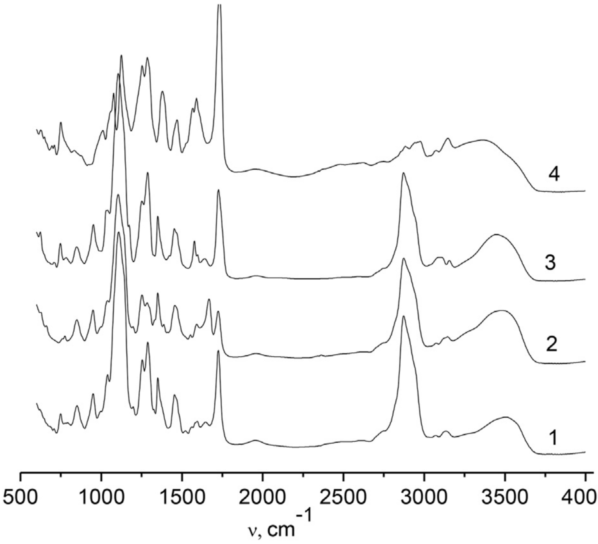

Fig. 8. IR spectra of protic carboxylate OILs: 1. $[MePEO\text{-}COO]^{-}[Hmim]^{+}$; 2. $[2MePEO\text{-}2COO]^{2-}2[Hmim]^{+}$; 3. $[PEO\text{-}2COO]^{2-}2[Hmim]^{+}$; 4. $[HBP\text{-}32COO]^{32-}32[Hmim]^{+}$.

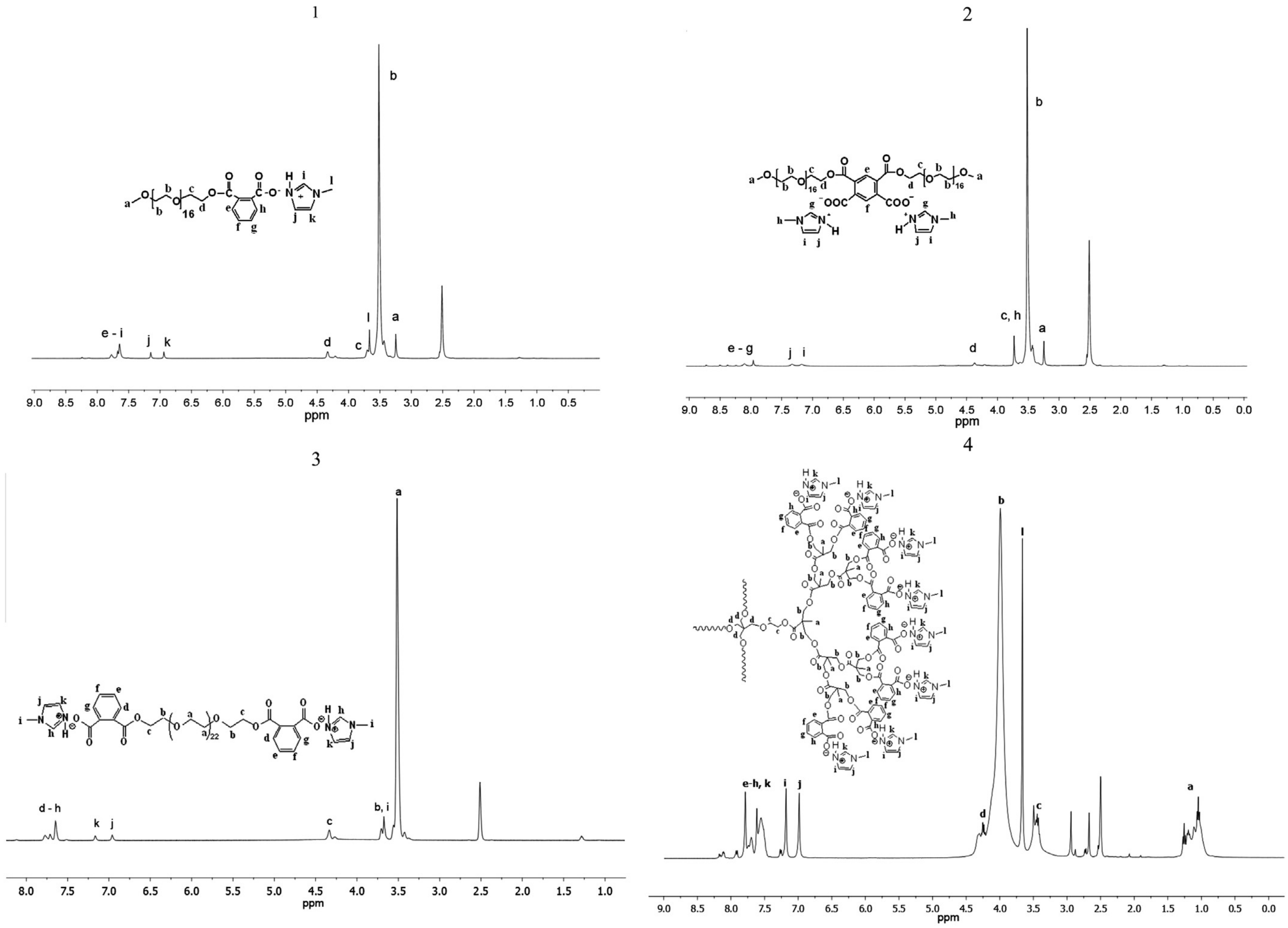

Fig. 9. ^{1}H NMR spectra of protic carboxylate OILs: 1. $[MePEO\text{-}COO]^-[Hmim]^+$; 2. $[2MePEO\text{-}2COO]^{2-}2[Hmim]^+$; 3. $[PEO\text{-}2COO]^{2-}2[Hmim]^+$; 4. $[HBP\text{-}32COO]^{32-}32[Hmim]^+$.

analogs are observed (Table 1). Similar trend can be seen when comparing hyperbranched aprotic $[HBP\text{-}32COO]^{32-}32[Mmim]^+$ and protic $[HBP\text{-}32COO]^{32-}32[Hmim]^+$ OILs (Table 1). It is reasonable to assume that the oligoester component in the case of aprotic $[HBP\text{-}32COO]^{32-}32[Mmim]^+$ compound is not so efficient ion conducting media as in the case of protic $[HBP\text{-}32COO]^{32-}32[Mmim]^+$ as well as linear protic and aprotic OILs containing oligoether component. This statement is also proved by the highest glass transition temperature (32.4 °C, Table 1) observed for $[HBP\text{-}32COO]^{32-}32[Mmim]^+$ compound. Let us note that cationic protic dendrimer OIL containing NH_3^+ Tf_2N^- groups ($T_m \sim -2.5$ °C) is characterized by the value of proton conductivity of $2.21 \cdot 10^{-3}$ at 24 °C [52].

4. Conclusions

We report on the method of synthesis of anionic protic and aprotic oligomeric ionic liquids (OIL) based on reaction of oligo(ethylene oxide)diol (MW 1000), its monomethyl ether (MW 750), and phthalic-, 2-sulfobenzoic anhydride and pyromellitic dianhydride with following neutralization of obtained oligomeric mono- and di-acids (carboxylic and sulfonic) with N-methylimidazole or its quaternated derivative. Hyperbranched anionic protic and aprotic OILs were synthesized in a similar fashion using corresponding branched poly(ester polyol) containing 32 hydroxyl groups. Depending on the nature of their ionic groups protic linear-chain OILs may be amorphous at room temperature or prone to form a low melting temperature crystalline phase. On the contrary, aprotic linear OILs (except linear OIL of a “butterfly structure”) and hyperbranched protic and aprotic OILs are amorphous. The type of

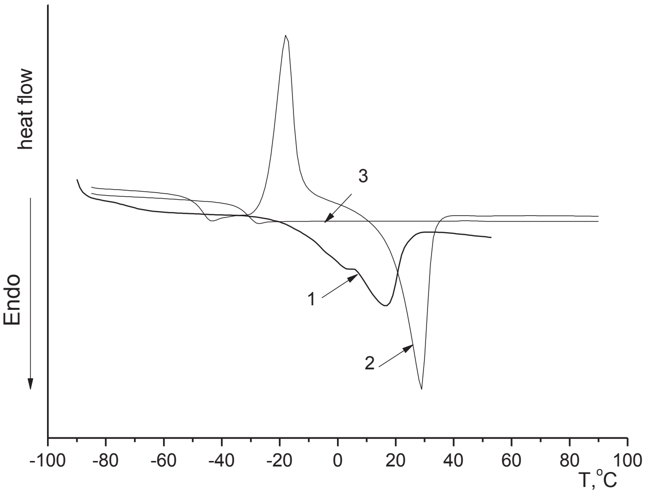

Fig. 10. The temperature dependence of heat flow for synthesized OILs: 1. $[MePEO\text{-}SO_3]^-$[Hmim2. $[PEO\text{-}2COO]^{2-}2[Hmim]^+$; 3. $[PEO\text{-}2SO_3]^{2-}2[Hmim]^+$.

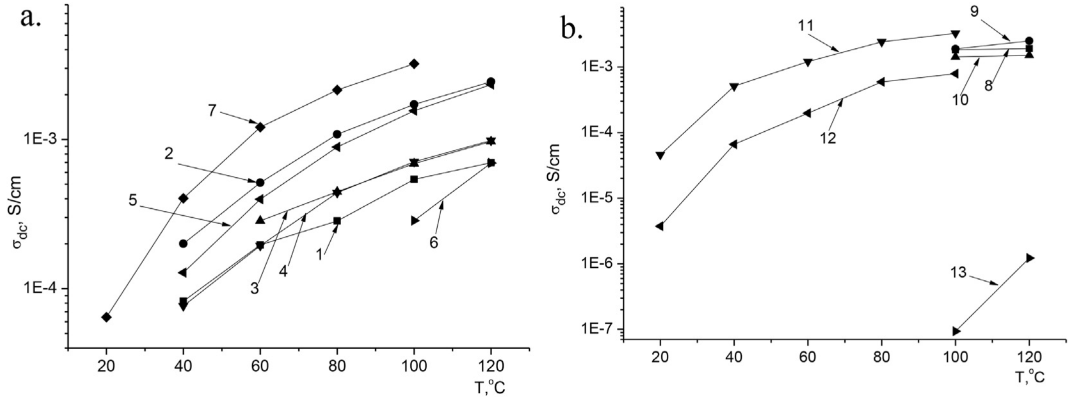

Fig. 11. Temperature dependence of ion conductivity of OILs. a. Protic OILs: 1. [MePEO-COO]$^-$[Hmim]$^+$; 2. [MePEO-SO$_3$]$^-$[Hmim]$^+$; 3. [2MePEO-2COO]$^{2-}$2[Hmim]$^+$; 4. [PEO-2COO]$^{2-}$2[Hmim]$^+$; 5. [PEO-2SO$_3$]$^{2-}$2[Hmim]$^+$; 6. [HBP-32COO]$^{32-}$32[Hmim]$^+$. 7. [HBP-32SO$_3$]$^{32-}$32[Hmim]$^+$; b. Aprotic OILs: 8. [MePEO-COO]$^-$[Mmim]$^+$; 9. [MePEO-SO$_3$]$^-$[Mmim]$^+$; 10. [2MePEO-2COO]$^{2-}$2[Mmim]$^+$; 11. [PEO-2COO]$^{2-}$2[Mmim]$^+$; 12. [PEO-2SO$_3$]$^{2-}$2[Mmim]$^+$; 13. [HBP-32COO]$^{32-}$32[Mmim]$^+$.

the ionic group is of a critical importance and determines thermal stability these OILs and their ionic conductivity properties in the range of 20–120 °C under anhydrous conditions. Particularly, we demonstrate the ionic conductivity of the order of 10^{-3} S/cm at temperatures 100–120 °C, which makes the synthesized materials attractive for practical applications.

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References

[1] Ohno H. Macromol Symp 2007;249–250(1):551–6.
[2] Green O, Grubjesic S, Lee S, Firestone MA. Polym Rev 2009;49(4):339–60.
[3] Green MD, Long TE. Polym Rev 2009;49(4):291–314.
[4] Mecerreyes D. Prog Polym Sci 2011;36(12):1629–48.
[5] Yuan J, Meccerreyes D, Antonietti M. Prog Polym Sci 2013;38(7):1009–36.
[6] Jaeger W, Bohrisch J, Laschewsky A. Prog Polym Sci 2010;35:511–77.
[7] Chapter 9 Shaplov AS, Lozinskaya EI, Vygodskii YS. Electrochemical properties and applications of ionic liquids. In: Torriero AAJ, Shiddiky M, editors. Polymer Ionic Liquids (PILs): synthesis, design and application in electrochemistry as ion conducting materials. New York: Nova Science Publishers Inc.; 2011.
[8] Shaplov AS, Ponkratov DO, Vlasov PS, Lozinskaya EI, Komarova LI, Malyshkina IA, et al. Polym Sci B 2013;55(3–4):122–38.
[9] Prescher S, Polzer F, Yang Y, Siebenbürger M, Ballauff M, Yuan J. J Am Chem Soc 2014;136(1):12–5.
[10] Mezhikovsky SM, Arinstein AE, Deberdeev RY. Oligomeric state of a substance: monograph. Moscow: Nauka; 2005 [in Russian].
[11] Kerscher B, Appel A-K, Thomann R, Mülhaupt R. Macromolecules 2013;46(11):4395–402.
[12] Imam MR, Peterca M, Edlund U, Balagurusamy VSK, Percec V. J Polym Sci Polym Chem 2009;47(16):4165–93.
[13] He X, Chan TH. Org Lett 2007;9(14):2681–4.
[14] Hallett JP, Welton T. Chem Rev 2011;111(5):3508–76.
[15] Bideau JL, Viau L, Vioux A. Chem Soc Rev 2011;40(2):907–25.
[16] Greaves TL, Drummond CJ. Chem Rev 2008;108(1):206–37.
[17] Nakai Y, Ito K, Ohno H. Solid State Ionics 1998;113–115:199–204.
[18] Ito K, Tominaga Y, Ohno H. Electrochim Acta 1997;42(10):1561–70.
[19] Ito K, Nishina N, Ohno H. J Mater Chem 1997;7(8):1357–62.
[20] Xu K, Angell CA. Electrochim Acta 1995;40(13–14):2401–3.
[21] Ohno H, Ito K. Polymer 1995;36(4):891–3.
[22] Tominaga Y, Mizumo T, Ohno H. Polym Adv Technol 2000;11(8–12):524–8.
[23] Lipatov YuS, Finerman AE, Shrubovich VA, Shevchenko VV. Reports Acad Sci USSR, Ser B 1984;10:41–4 [in Russian].
[24] Lipatov YuS, Finerman AE, Shevchenko VV, Shrubovich VA. Polym Sci 1987;29(3):562–6 [in Russian].
[25] Lipatov YuS, Shevchenko VV, Shrubovich VA, Vasilyevskaya GA, Klimenko NS, Finerman AE. Reports Acad Sci USSR 1989;306(2):360–4 [in Russian].
[26] Lipatov YuS, Shevchenko VV, Feinerman AE. Ukrainian Polym J 1993;2(2):85–97.
[27] Lipatov YuS, Shilov VV, Dmitruk NV, Tsukruk VV, Polyatskova NV, Shevchenko VV, et al. Colloid J 1984;46(4):691–9 [in Russian].
[28] Shevchenko VV, Klimenko NS, Shevchuk AV, Peleshanko SA, Vortman MYa, Privalko EG, et al. Polym J 2006;28(1):42–5 [in Russian].
[29] Kato K-I, Ito-Akita K, Ohno H. J Solid State Electrochem 2000;4(3):141–5.
[30] Yoshizawa M, Ohno H. Electrochim Acta 2001;46(10–11):1723–8.
[31] Wang Y, Luo J, Zuliang L. J Organomet Chem 2013;739:1–5.
[32] Wang M, Xiao X, Zhou X, Li X, Lin Y. Sol Energ Mater Sol Cell 2007;91(9):785–90.
[33] Seo D-W, Sarker S, Chandra Deb Nath N, Choi S-W, Saleh Ahammad AJ, Lee J-J, et al. Electrochim Acta 2010;55(4):1483–8.
[34] Ito K, Nishina N, Ohno H. Electrochim Acta 2000;45(8–9):1295–8.
[35] Luo L, Yu N, Tan R, Jin Y, Yin D. Catal Lett 2009;130(3–4):489–95.
[36] Wang M, Lin Y, Zhou X. Mater Chem Phys 2008;107(1):61–6.
[37] Stalgren JJR, Pamedytyte V, Makuska R, Claesson PM, Brown W, Jacobsson U. Polym Int 2003;52(3):399–405.
[38] Stathatos E, Jovanovski V, Orel B, Jerman I, Lianos P. J Phys Chem C 2007;111(17):6528–32.
[39] Jovanovski V, Orel B, Ješe R, Vuk AŠ, Mali G, Hočevar SB, et al. J Phys Chem B 2005;109(30):14387–95.
[40] Tan J, Ma D, Sun X, Feng S, Zhang C. Dalton Trans 2013;42(13):4337–9.
[41] Jeon J-H, Tanaka K, Chujo Y. RSC Adv 2013;3(7):2422–7.
[42] Tanaka K, Ishiguro F, Chujo Y. J Am Chem Soc 2010;13(50):17649–51.
[43] Tanaka K, Chujo Y. Polym J 2013;45(3):247–54.
[44] Castriciano MA, Leone N, Cardiano P, Manickam S, Scolaro LM, Lo Schiavo S. J Mater Chem C 2013;1(31):4746–53.
[45] Liu Y, Leng C, Chisholm B, Stafslien S, Majumdar P, Chen Z. Langmuir 2013;29(9):2897–905.
[46] Cardiano P, Lazzara G, Manickam S, Mineo P, Milioto S, Lo Schiavo S. Eur J Inorg Chem 2012;34:5668–76.
[47] Čolović M, Jerman I, Gaberšček M, Orel B. Sol Energy Mater Sol Cell 2011;95(12):3472–81.
[48] Tanaka K, Ishiguro F, Chujo Y. Polym J 2011;43(8):708–13.
[49] Schwab E, Mecking S. J Polym Sci Polym Chem 2005;43(19):4609–17.
[50] Du Y, Chen Q, Shen L, Xing Y, Dai J. J Appl Polym Sci 2011;121(5):2927–35.
[51] Mchedlov-Petrossyan NO, Bryleva EYu, Vodolazkaya NA, Dissanayake AA, Ford WT. Langmuir 2008;24(11):5689–99.
[52] Huang JF, Luo H, Liang C, Sun IW, Baker GA, Dai S. J Am Chem Soc 2005;127(37):12784–5.
[53] Zoller U. Tetrahedron 1988;44(24):7413–26.
[54] Chen KM, Wang UR. J Am Oil Chem Soc 1992;69(1):60–3.
[55] Matsuda H. J Cell Plast 1982;18(2):114–20.
[56] Bellamy L. Infrared spectra of complex molecules. Moscow: Foreign Literature Publishing House; 1963 [in Russian].
[57] Pretsch E, Bühlmann Ph, Badertscher M. Structure determination of organic compounds. Tables of spectral data. 4th, revised and enlaged edition. Berlin: Springer-Verlag Berlin Heidelberg; 2009.
[58] Menczel JD, Prime RB. Thermal analysis of polymers. Fundamentals and applications. New-York: WILEY; 2009.
[59] Kyritsis A, Pissis P, Grammatikakis J. J Polym Sci B Polym Phys 1995;33(12):1737–50.