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SYNTHESIS

Amphiphilic Protic Anionic Oligomeric Ionic Liquids of Hyperbranched Structure

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Abstract—The method of synthesizing anionic amphiphilic protic hyperbranched ionic liquids with the controlled ratio between hydrophilic ionic-liquid groups and hydrophobic alkyl urethane fragments in the oligoester nucleus shell is developed. These compounds are synthesized by the interaction of excess hyperbranched polyesterpolyol containing 32 terminal hydroxyl groups with *n*-octadecyl isocynate followed by the acylation of hydroxyl groups by phthalic anhydride or 2-sulfobenzoic anhydride and the neutralization of the formed carboxyl or sulfonic groups by *N*-methylimidazole or 1,2,4-1H-triazole. With a rise in the content of alkyl urethane fragments, the synthesized compounds form the crystalline phase. Structuring of the system leads to different effects of the degree of ionicity of ionic-liquid groups on proton conductivity, which is within 10^{-7}–10^{-4} S/cm at 100–120°C under anhydrous conditions. The thermal stability of the hyperbranched ionic liquids is determined by the nature of ionic-liquid groups and the amount of the introduced alkyl urethane fragments; it is in the range of 170–270°C.

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INTRODUCTION

Nowadays organic ionic liquids, which represent liquid or low-melting organic salts (with $T_m < 100°C$), are more and more attractive in terms of polymer science and practice because of their unique properties [1–3]. The latter are determined by the chemical nature of salt groups which are formed using a substantially expanded scope of organic cations and organic and inorganic anions at their different combinations. In the literature, these groups are called "ionic-liquid groups", "ionic-liquid functionalities", or "imidazolium-type ionic compounds" [4–6].

Polymer analogs synthesized from reactive ionic liquids made it possible to combine their unique properties with the macroproperties of polymer systems [7, 8]; this initiated the emergence of a new direction in the field of polyelectrolytes [5, 9–11]. These compounds are promising for use in both traditional and new areas of application of polyelectrolytes [9–12].

However, these compounds lose with rare exception (e.g., [13]) the ability to exist in the liquid state in a wide temperature range [10–12]. The oligomeric ionic liquids hold an intermediate position between the low-molecular-weight liquids and their polymer analogs in terms of molecular weight. As the former compounds, they are divided into protic and aprotic; as the latter ones, they are divided into anionic and cationic [14, 15].

On the basis of the molecular architecture of the oligomer chain, the main types of ionic liquids are as follows: linear, starlike and comblike organosilicon ionic liquids and dendritic oligomeric ionic liquids [11, 14, 15]. In terms of practical use, they are interesting above all as ion-conducting media for different electrochemical devices and as building blocks for the synthesis of block copolymers, photoluminescent materials, biomedical materials, heterogeneous catalysts, complex-forming compounds, functional additives for composite materials, etc.

A wide structural potential of ionic-liquid groups in combination with a substantial influence of oligomer terminal groups on their structure and properties opens new ways for tuning the properties of this type of high-molecular-weight compounds [16].

In this respect, of special interest are oligomeric liquids of hyperbranched structure among dendritic ionic liquids [11, 14, 15]. A high density of terminal functional groups in these globular structures opens great opportunities for the targeted change in their structure and properties, such as the combination of ionic-liquid groups of different chemical natures in one molecule and their further modification while preserving their liquid state in a wide temperature range.

Owing to their globular structure, amphiphilicity, and polyfunctionality, the oligomeric ionic liquids of the hyperbranched structure have significant advantages over their linear analogs in terms of molecular self-organization [11]. They show aggregation stability and the ability to form a wider range of structures of ordered and labile phases in solution and at the interface in response to external stimuli. Of special interest is the formation of such ordered structures as liquid crystals, micelles, and vesicles [17–21].

In this direction, protic and aprotic amphiphilic oligomeric hyperbranched ionic liquids of solely cationic type are the main object of synthesis and characterization. In these compounds, the hyperbranched nucleus itself is hydrophobic, while ionic-liquid groups at the periphery compose the hydrophilic part. At the same time, the hydrophilic-hydrophobic balance was controlled both by the introduction of covalently bonded hydrophilic oxyethylene fragments on the external shell of nucleus and via the binding of hydrophobic anionogenic compounds, including long-chain aliphatic (C_6–C_{18}), aliphatic-aromatic, and aromatic carboxylated, sulfonate and sulfate. With this approach a certain physical function ensuring liquid-crystalline properties of such a system may be imparted to the introduced hydrophobic constituent. Polyesters, polyglycerol, polyoxetane, polylysine, polyamidoimine, polyethyleneimine, and polypropyleneimine were used as hyperbranched nuclei in these compounds [4, 17–19, 21–29].

In the above-considered hyperbranched oligomeric ionic liquids, ionic-liquid groups are terminal on branching chains. In [20], a new type of polymer soaps—hyperbranched polymer ionic liquids of ionene type—was described. In these compounds, ionic-liquid groups occur in main branching chains and aliphatic tertiary amino groups are terminal ones. In addition, hyperbranched ionomers containing aprotic ionic-liquid groups in the side part of branching chains were synthesized via the direct catalytic copolymerization of ethylene with tetraalkylammonium ionic-liquid comonomers of the acrylate type [30].

The first protic hyperbranched oligomeric ionic liquids of the anionic type were synthesized in [14]: carboxyl or sulfone groups were fixed on the shell of the hyperbranched polyesterpolyol followed by their neutralization by *N*-methylimidazole. The effect of the ionic-liquid group nature on structure formation and ionic conductivity of these compounds was ascertained.

With the aim to expand the possibilities to control the amphiphilic properties of this type of ionic liquids and their self-organization ability, the present work suggests a new method for the synthesis of protic anionic hyperbranched oligomeric ionic liquids, whose hydrophobic properties are amplified by the introduction of long-chain alkyl urethane fragments into the nucleus at their adjustable ratio with hydrophilic carboxylate and sulfonate groups with imidazole and triazole counterions. The thermophysical properties of these compounds and their proton conductivity under anhydrous conditions were investigated.

EXPERIMENTAL

N-Methylimidazole (99%), *n*-octadecyl isocyanate (98%), cyclic anhydride of 2-sulfobenzoic acid (90%, Aldrich), and 1,2,4-1H-triazole (99.5%, Acros) were used as received. The hyperbranched aliphatic oligoesterpolyol of the third generation based on etoxylated pentaerythritol and 2,2-dimethylolpropionic acid containing 32 terminal hydroxyl groups in the nucleus (HBP-OH) (Boltorn® H30, Perstorp, Sweden) [31] was reprecipitated from DMF in ether followed by vacuum drying at 25–30°C for 6 h. The content of OH groups determined by acylation was 14.5%. This value corresponds to the equivalent MM of the oligomer equal to 117 g-equiv. Phthalic anhydride was purified via sublimation. DMF, diethyl ether, acetone, isopropanol, and acetonitrile were distilled before use. The content of acidic groups in the hyperbranched carboxyl and sulfone derivatives synthesized at the intermediate stage was determined by the reverse acid-base titration [32].

Synthesis of Hyperbranched Amphiphilic Oligomeric Carboxylic Acids (HBP Is Hyperbranched Polyester)

$(C_{18}H_{37})_8$–HBP–$(COOH)_{24}$. *n*-Octadecyl isocyanate (2.444 g, 0.0083 g-equiv) was added to the solution HBP-OH (3.877 g, 0.0331 g-equiv) in DMF (14 mL) at 80°C, and the reaction was conducted for 12 h until disappearance of isocyanate groups (IR data). After that phthalic anhydride (3.679 g, 0.0249 g-equiv) was added to the resulting solution, which was heated at 80°C for 20 h as described in [14]. The solvent was partially removed at a reduced pressure, and the final product was reprecipitated from acetone in hexane and dried at 40–50°C. The yield was 7.48 g (74.8%); the content of COOH groups was 10.2% (calculated, 11.2%). The product was a transparent light brown viscous compound well soluble in acetone, ethyl acetate, chloroform, and DMF and insoluble in acetonitrile and hexane.

$(C_{18}H_{37})_{16}$–HBP–$(COOH)_{16}$ acid was obtained by the above technique via the interaction of HBP-OH (3.46 g, 0.0295 g-equiv) with *n*-octadecyl isocyanate (4.357 g, 0.0147 g-equiv) in DMF (15 mL) followed by acylation of the reaction product by phthalic anhydride (2.186 g, 0.0147 g-equiv). The yield was 6.02 g (60.2%); the amount of COOH groups was 6.5% (calculated, 6.7%). The product was a transparent light brown solid well soluble in acetone, benzene, ethyl acetate, THF, chloroform, and DMF and insoluble in acetonitrile, hexane, and water.

$(C_{18}H_{37})_{24}$–HBP–$(COOH)_8$ was synthesized by a similar technique via the reaction of HBP-OH (3.118 g, 0.0266 g-equiv) with *n*-octadecyl isocyanate (5.896 g, 0.0200 g-equiv) in DMF (16 mL) followed by acylation of the synthesized compound by phthalic anhydride (0.986 g, 0.0067 g-equiv). The solvent was partially removed under a reduced pressure, and the final product was washed with acetone and dried at 40–50°C. The yield was 6.24 g (calculated, 62.4%); the content of COOH groups was 2.8% (calculated, 3.0%). The product was a light brown viscous compound well soluble in hexane, ethyl alcohol, and DMF and insoluble in acetone and water.

$(C_{18}H_{37})_{16}$–HBP–$(SO_3H)_{16}$. HBP (1.149 g, 0.0098 g-equiv) in DMF (8 mL) was added to *n*-octadecyl isocyanate (1.448 g, 0.0049 g-equiv) at 80°C, and the reaction mixture was stirred for 12 h until consumption of isocyanate groups (IR data). Then the cyclic anhydride of 2-sulfobenzoic acid (0.903 g, 0.0049 g-equiv) was added to the resulting solution, and the reaction mixture was stirred for 20 h at 80°C. The solvent was partially removed under a reduced pressure (1–3 mm Hg), and the resulting product was precipitated from acetone in acetonitrile and dried at 40–50°C until a constant mass. The yield was 1.709 g (48.8%). According to the acid-base titration [32], the content of sulfonic groups was 10.8% (calculated, 11.4%). The product was a light brown solid compound readily soluble in water, DMF, and DMSO and insoluble in acetonitrile and hexane.

Synthesis of Amphiphilic Hyperbranched Anion-Active Protic Oligomeric Ionic Liquids

The oligomeric ionic liquid **$(C_{18}H_{37})_8$–HBP–$([COO]^-[HMim]^+)_{24}$** was obtained by the neutralization of $(C_{18}H_{37})_8$–HBP–$(COOH)_{24}$ acid (1.69 g, 0.0038 g-equiv) by *N*-methylimidazole (0.31 g, 0.038 g-equiv) in ethanol (5 mL) under stirring for 3–5 min at room temperature. The solvent was partially evaporated, and the product was precipitated in ether. The resulting oligomeric ionic liquid was dried at 40–50°C. The yield was 1.31 g (65.5%). The product was a transparent light brown viscous liquid well soluble in acetone, chloroform, THF, DMF, and DMSO and insoluble in ether, benzene, and ethyl acetate. IR: ν C–O–C, ν C–O of carboxylate groups (1026–1342 cm^{-1}), δ sym CH_3 (1373 cm^{-1}), δ CH_2, as CH_3 (1470 cm^{-1}), ν ar C–C (1499–1655 cm^{-1}), ν C=O (1732 cm^{-1}), overtones of N–H bonds of heterocycles (1860–2170 cm^{-1}), ν N–H$^+$ (2350–2675 cm^{-1}), ν al C–H (2770–3041 cm^{-1}), ν ar C–H (3072 cm^{-1}), ν C–H of imidazole cation (3146 cm^{-1}) [33]. ^{1}H NMR (DMSO-*d*$_6$): δ_H 0.79–0.90 (**CH_3**–CH_2–), 1.11 (**CH_3**–C), 0.94–1.48 (–**CH_2**–), 2.97–3.86 ((–**CH_2**–, –C**CH_2**O**CH_2**CH_2OC(O)–), 3.82 (–N(C**H_3**)–), 3.87–4.51 (–C**H_2**OC(O)–), 7.08 (–NH$^+$–CH=**CH**–N(CH_3)–), 7.26 (–NH$^+$–**CH**=CH–N(CH_3)–), 7.35–7.76, 8.11–8.27 (–Ar–**H**, –NH$^+$=**CH**–N(CH_3)–), 8.50 (–NH$^+$–**CH**=NH–) ppm. ^{13}C NMR ($CDCl_3$): δ_C 14.16 (**CH_3**–CH_2–), 17.45 (**CH_3**–C–), 22.71 (CH_3–**CH_2**–CH_2–), 26.83, 29.37, 29.73, 31.95, 35.33 (–CH_2–**CH_2**–CH_2–), 35.03 (–N–**CH_3**), 41.18 (–C(O)–NH–**CH_2**–CH_2–), 48.51 (–**C**(CH_3)(CH_2–)), 65.69–77.38 (–**CH_2**–O–), 121.81, 122.37 (–NH–**CH**=CH–), 128.85, 131.21, 132.44, 133.76, 136.21 (–CH=**CH**–CH=), 171.54 (>**C**=O) ppm.

The oligomeric ionic liquid **$(C_{18}H_{37})_8$–HBP–$([COO]^-[HTri]^+)_{24}$**, which was synthesized by a similar technique using 1,2,4-1H-triazole as a base, was a transparent light brown viscous liquid well soluble in DMF, DMSO, ethanol, chloroform, and THF and insoluble in benzene and ether. The yield was 0.97 g (48.5%). IR: ν C–O–C, ν C–O of the carboxylate groups (1028–1344 cm^{-1}), δ sym CH_3 (1373 cm^{-1}), δ CH_2, as CH_3 (1470 cm^{-1}), ν ar C–C (1500–1639 cm^{-1}), ν C=O (1734 cm^{-1}), overtones of N–H bonds of heterocycles (1832–2162 cm^{-1}), ν N–H$^+$ (2350–2688 cm^{-1}), ν al C–H (2800–3020 cm^{-1}), ν ar C–H of heterocycle (3072 cm^{-1}). ^{1}H NMR (DMSO-*d*$_6$): δ_H 0.75–0.90 (**CH_3**–CH_2–), 1.11 (**CH_3**–C), 0.90–1.51 (–**CH_2**–), 2.57–3.88 ((–**CH_2**–, –C**CH_2**O**CH_2**CH_2OC(O)–), 3.88–4.70 (–**CH_2**OC(O)–), 7.29–8.79 (–Ar–**H**, –NH=**CH**–NH–) ppm. ^{13}C NMR ($CDCl_3$): δ_C 14.16 (**C**H_3–CH_2–), 17.41 (**C**H_3–C–), 22.71 (CH_3–**C**H_2–CH_2–), 23.88, 26.80, 29.37, 29.73, 31.94, 32.12, 35.28 (–CH_2–**C**H_2–CH_2–), 41.19 (–C(O)–NH–**C**H_2–CH_2–), 46.46, 48.47 (–**C**(CH_3)(CH_2–)), 64.33, 65.96, 69.87, 76.76, 77.08, 77.39 (–C–**C**H_2–O–), 89.00 (**C**(CH_2–)$_4$), 128.88, 130.74, 131.27, 132.89, 140.63, 142.18, 145.78, 151.67 (–CH=**CH**–CH=, –NH–**CH**=CH–), 162.80, 173.56 (>**C**=O) ppm.

The oligomeric ionic liquid **$(C_{18}H_{37})_{16}$–HBP–$([COO]^-[HMim]^+)_{16}$** was obtained by the neutralization of $(C_{18}H_{37})_{16}$–HBP–$(COOH)_{16}$ acid (1.79 g, 0.0026 g-equiv) by *N*-methylimidazole (0.21 g, 0.0026 g-equiv) in ethanol (6 mL) under stirring for 3–5 min at room temperature. The solvent was partially evaporated, and the product was precipitated in acetonitrile. The resulting oligomeric ionic liquid was dried at 40–50°C. The yield was 1.47 g (73.3%). The product was a transparent light brown viscous liquid well soluble in acetone, ethyl acetate, benzene, chloroform, DMF, DMSO, and THF and insoluble in acetonitrile. IR: ν C–O–C, ν C–O of carboxylate groups (1028–1345 cm^{-1}), δ sym CH_3 (1375 cm^{-1}), δ CH_2, as CH_3 (1468 cm^{-1}), ν ar C–C (1500–1640 cm^{-1}), ν C=O (1732 cm^{-1}), overtones of N–H bonds of heterocycles (1825–2200 cm^{-1}), ν N–H$^+$ (2300–2670 cm^{-1}), ν al C–H (2800–3025 cm^{-1}), ν ar C–H (3070 cm^{-1}), ν C–H of imidazole cation (3145 cm^{-1}) [33]. ^{1}H NMR (DMSO-d_6); δ_H 0.66–0.88 ($\mathbf{CH_3}$–CH_2–), 1.04 ($\mathbf{CH_3}$–C), 0.91–1.40 (–$\mathbf{CH_2}$–), 3.35–3.53 (–C$\mathbf{CH_2}$O$\mathbf{CH_2}$$CH_2$OC(O)–), 3.66 (–N($\mathbf{CH_3}$)–), 3.91–4.41 (–$\mathbf{CH_2}$OC(O)–), 6.98 (–NH$^+$–CH=$\mathbf{CH}$–N($CH_3$)–), 7.18 (–NH$^+$–$\mathbf{CH}$=CH–N($CH_3$)–), 7.47–8.14 (–Ar–$\mathbf{H}$, –NH$^+$=$\mathbf{CH}$–N($CH_3$)–), 8.07 (–NH$^+$–$\mathbf{CH}$=NH–) ppm.

The oligomeric ionic liquid **$(C_{18}H_{37})_{16}$–HBP–$([COO]^-[HTri]^+)_{16}$**, which was synthesized by the similar technique using 1,2,4-triazole as a base, was a transparent light brown viscous liquid well soluble in acetone, ethyl acetate, chloroform, DMF, DMSO, and THF and insoluble in acetonitrile and water. The yield was 1.60 g (79.8%). IR: ν C–O–C, ν C–O of carboxylate groups (1028–1348 cm^{-1}), δ sym CH_3 (1371 cm^{-1}), δ CH_2 (1468 cm^{-1}), ν ar C–C (1499–1614 cm^{-1}), ν C=O (1731 cm^{-1}), overtones of N–H bonds of heterocycles (1825–2150 cm^{-1}), ν N–H$^+$ (2350–2700 cm^{-1}), ν al C–H (2800–3030 cm^{-1}), ν ar C–H (3072 cm^{-1}), ν C–H of heterocycle (3136 cm^{-1}) [33]. ^{1}H NMR (DMSO-d_6): δ_H 0.71–0.88 ($\mathbf{CH_3}$–CH_2–), 1.04 ($\mathbf{CH_3}$–C), 0.88–1.54 (–$\mathbf{CH_2}$–), 2.78–3.65 ((–$\mathbf{CH_2}$–, –C$\mathbf{CH_2}$O$\mathbf{CH_2}$$CH_2$OC(O)–), 2.78–4.50 (–$\mathbf{CH_2}$OC(O)–), 6.68–8.56 (–Ar–$\mathbf{H}$, –NH=$\mathbf{CH}$–NH–) ppm.

The oligomeric ionic liquid **$(C_{18}H_{37})_{24}$–HBP–$([COO]^-[HMim]^+)_8$** was obtained by the neutralization of 1.90 g (0.0012 g-equiv) of $(C_{18}H_{37})_{24}$–HBP–$(COOH)_8$ acid by *N*-methylimidazole (0.09 g, 0.0012 g-equiv) in isopropanol (8 mL). The solvent was partially evaporated, and the product was precipitated in acetonitrile. The resulting oligomeric ionic liquid was dried at 40–50°C. The yield was 1.72 g (86.2%). The product was a transparent light brown solid with a temperature of transition to the liquid state of 55–65°C well soluble in benzene, chloroform, DMF, DMSO, and THF and insoluble in acetonitrile, water, and ethanol. IR: ν C–O–C, ν C–O of carboxylate groups (1028–1348 cm^{-1}), δ sym CH_3 (1377 cm^{-1}), δ CH_2, as CH_3 (1468 cm^{-1}), ν ar C–C (1493–1642 cm^{-1}), ν C=O (1740 cm^{-1}), ν N–H$^+$ (2360–2698 cm^{-1}), ν al C–H (2800–3041 cm^{-1}), ν ar C–H (3072 cm^{-1}), ν C–H of imidazole cation (3149 cm^{-1}) [33]. ^{1}H NMR (DMSO-d_6): δ_H 0.77–0.97 ($\mathbf{CH_3}$–CH_2–), 1.17 ($\mathbf{CH_3}$–C), 1.03–1.95 (–$\mathbf{CH_2}$–), 2.97–3.93 ((–$\mathbf{CH_2}$–,–C$\mathbf{CH_2}$O$\mathbf{CH_2}$$CH_2$OC(O)–), 3.83 (–N($\mathbf{CH_3}$)–), 3.95–4.59 (–$\mathbf{CH_2}$OC(O)–), 7.01 (–NH$^+$–CH=$\mathbf{CH}$–N($CH_3$)–), 7.44–8.34 (–Ar–$\mathbf{H}$, –NH$^+$=$\mathbf{CH}$– N($CH_3$)–), 8.27 (–NH$^+$–$\mathbf{CH}$=NH–) ppm. ^{13}C NMR ($CDCl_3$): δ_C 14.16 ($\mathbf{CH_3}$–CH_2–), 17.61 ($\mathbf{CH_3}$–C–), 22.72 (CH_3–$\mathbf{CH_2}$–CH_2–), 26.86, 29.40, 29.75, 31.96, 41.21 (–C(O)–NH–$\mathbf{CH_2}$–CH_2–), 46.67, 48.45 (–$\mathbf{C}$(CH_3)(CH_2–)), 64.51–66.32 (–C–$\mathbf{CH_2}$–O–), 131.25, 132.68 (–C=$\mathbf{C}$–C=), 156.14, 172.47, 173.30 (>$\mathbf{C}$=O) ppm.

The oligomeric ionic liquid **$(C_{18}H_{37})_{24}$–HBP–$([COO]^-[HTri]^+)_8$**, which was synthesized according to a similar technique using 1,2,4-triazole as a base, was a transparent light brown solid with a temperature of transition to the liquid state of 55–65°C, well soluble in benzene, chloroform, DMF, DMSO, and THF, and insoluble in acetonitrile, water and ethanol. The yield was 1.63 g (81.3%). IR: ν C–O–C, ν C–O of carboxylate groups (1028–1350 cm^{-1}), δ sym CH_3 (1375 cm^{-1}), δ CH_2, as CH_3 (1468 cm^{-1}), ν ar C–C (1492–1641 cm^{-1}), ν C=O (1736 cm^{-1}), ν al C–H (2800–3025 cm^{-1}), ar C–H (3065 cm^{-1}), ν C–H of heterocycle (3150 cm^{-1}), ν N–H$^+$ (2360 cm^{-1}) [33]. ^{1}H NMR (DMSO-d_6): δ_H 0.78–0.95 ($\mathbf{CH_3}$–CH_2–), 1.17 ($\mathbf{CH_3}$–C), 1.03–1.65 (–$\mathbf{CH_2}$–), 2.97–3.88 ((–$\mathbf{CH_2}$–, –C$\mathbf{CH_2}$O$\mathbf{CH_2}$$CH_2$OC(O)–), 3.88–4.56 (–$\mathbf{CH_2}$OC(O)–), 7.37–8.27 (–Ar–$\mathbf{H}$, –NH=$\mathbf{CH}$–NH–) ppm. ^{13}C NMR ($CDCl_3$): δ_C 14.16 ($\mathbf{CH_3}$–CH_2–), 17.52 ($\mathbf{CH_3}$–C–), 22.72 (CH_3–$\mathbf{CH_2}$–CH_2–), 26.86, 29.40, 29.75, 31.96, 41.23 (–C(O)–NH–$\mathbf{CH_2}$–CH_2–), 46.94, 48.66 (–$\mathbf{C}$(CH_3)(CH_2–)), 64.63–70.41(–C–$\mathbf{CH_2}$–O–), 131.20, 156.12 (–C=$\mathbf{C}$–C=), 169.05, 172.32 (>$\mathbf{C}$=O) ppm [33].

Synthesis of Amphiphilic Hyperbranched Sulfonate Protic Oligomeric Ionic Liquids

The oligomeric ionic liquid **$(C_{18}H_{37})_{16}$–HBP–$([SO_3]^-[HMim]^+)_{16}$** was synthesized by the neutralization of $(C_{18}H_{37})_{16}$–HBP–$(SO_3H)_{16}$ acid (1.803 g, 0.0024 g-equiv) with *N*-methylimidazole (0.197 g, 0.0024 g-equiv) in THF (5 mL) under stirring for 3–5 min at room temperature. The solvent was partially evaporated, and the product was precipitated in acetonitrile. The resulting oligomeric ionic liquid was dried at 40–50°C until a constant mass. The yield was 1.776 g (88.8%). The product was a pale yellow solid with a temperature of transition to the plastic state of 55–65°C well soluble in acetone, chloroform, benzene, THF, DMF, and DMSO and insoluble in ether and acetonitrile. IR: ν S=O (1019 cm^{-1}), ν C–O–C, ν C–O of ester groups (1031– 1352 cm^{-1}), δ sym CH_3 (1379 cm^{-1}), δ CH_2, as CH_3 (1469 cm^{-1}), ν ar C–C (1496–1650 cm^{-1}), ν C=O (1734 cm^{-1}), ν al C–H (2800–3025 cm^{-1}), ν ar C–H (3072 cm^{-1}), ν C–H of imidazole cation (3152 cm^{-1}) [33]. ^{1}H NMR (DMSO-d_6): δ_H 0.76–0.94 ($\mathbf{CH_3}$–), 1.43 ($\mathbf{CH_3}$–C), 0.94–1.95 (–$\mathbf{CH_2}$–), 2.45–3.85 ((–$\mathbf{CH_2}$–, –C$\mathbf{CH_2}$O$\mathbf{CH_2}$$CH_2$OC(O)–), 3.73 (–N($\mathbf{CH_3}$)–), 3.86–4.71 (–$\mathbf{CH_2}$OC(O)–), 7.06 (–NH$^+$–CH=$\mathbf{CH}$–N($CH_3$)–), 7.19 (–NH$^+$–$\mathbf{CH}$=CH–N($CH_3$)–), 7.27–7.55,7.75–8.22 $(-\mathrm{Ar}{-}\mathbf{H},\ -\mathrm{NH}^+{=}\mathbf{CH}{-}\mathrm{N(CH_3)}-)$, 8.35 $(-\mathrm{NH}^+{-}\mathbf{CH}{=}\mathrm{NH}-)$ ppm. ^{13}C NMR ($\mathrm{CDCl_3}$): δ_C 14.16 $(\mathbf{C}\mathrm{H_3{-}CH_2}-)$, 17.53 $(\mathbf{C}\mathrm{H_3{-}C}-)$, 22.72 $(\mathrm{CH_3}{-}\mathbf{C}\mathrm{H_2{-}CH_2}-)$, 26.86, 29.40, 29.75, 31.95, 35.33 $(-\mathrm{CH_2}{-}\mathbf{C}\mathrm{H_2{-}CH_2}-)$, 35.08 $(-\mathrm{N}{-}\mathbf{C}\mathrm{H_3})$, 41.18 $(-\mathrm{C(O){-}NH}{-}\mathbf{C}\mathrm{H_2{-}CH_2}-)$, 46.67, 48.64 $(-\mathbf{C}\mathrm{(CH_3)(CH_2}-))$, 63.12–70.32 $(-\mathrm{C}{-}\mathbf{C}\mathrm{H_2{-}O}-)$, 121.79, 122.88, 127.92, 130.45 $(-\mathrm{C}{=}\mathbf{C}{-}\mathrm{C}{=})$, 136.45 $(-\mathrm{NH}{-}\mathbf{C}\mathrm{H{=}N}-)$, 172.48 $(-\mathbf{C}{=}\mathrm{O})$ ppm [33].

The oligomeric ionic liquid $\mathbf{(C_{18}H_{37})_{16}{-}HBP{-}([SO_3]^-[HTri]^+)_{16}}$ was synthesized in a similar manner using 1,2,4-1H-triazole as a base. The resulting compound was a dark brown solid with a temperature of transition to the liquid state of 55–65°C easily soluble in chloroform, benzene, DMF, DMSO, and THF and insoluble in ethanol and acetonitrile. The yield was 0.623 g (89.5%). IR: ν S=O (1019 cm^{-1}), ν C–O–C, ν C–O of ester groups (1031–1352 cm^{-1}), δ sym $\mathrm{CH_3}$ (1374 cm^{-1}), δ $\mathrm{CH_2}$, as $\mathrm{CH_3}$ (1469 cm^{-1}), ν ar C–C (1501–1650 cm^{-1}), ν C=O (1735 cm^{-1}), ν $\mathrm{N{-}H^+}$ (2350–2700 cm^{-1}), ν al C–H (2800–3029 cm^{-1}), ar C–H (3068 cm^{-1}), C–H of heterocycle (3129 cm^{-1}) [33]. ^{1}H NMR (DMSO-d_6): δ_H 0.80–0.92 $(\mathrm{C}\mathbf{H}_3-)$, 1.43 $(\mathrm{C}\mathbf{H}_3{-}\mathrm{C})$, 0.93–1.72 $(-\mathrm{C}\mathbf{H}_2-)$, 2.45–3.88 $(-\mathrm{C}\mathbf{CH_2}\mathrm{O}\mathbf{CH_2}\mathrm{CH_2OC(O)}-)$, 3.88–5.74 $(-\mathbf{CH_2}\mathrm{OC(O)}-)$, 7.28–8.43 $(-\mathrm{Ar}{-}\mathbf{H},\ -\mathrm{NH}{=}\mathbf{CH}{-}\mathrm{NH}-)$ ppm. ^{13}C NMR ($\mathrm{CDCl_3}$): δ_C 14.15 $(\mathbf{C}\mathrm{H_3{-}CH_2}-)$, 17.39 $(\mathbf{C}\mathrm{H_3{-}C}-)$, 22.72 $(\mathrm{CH_3}{-}\mathbf{C}\mathrm{H_2{-}CH_2}-)$, 23.89, 26.84, 29.39, 29.74, 31.95, 35.31 $(-\mathrm{CH_2}{-}\mathbf{C}\mathrm{H_2{-}CH_2}-)$, 41.21 $(-\mathrm{C(O){-}NH}{-}\mathbf{C}\mathrm{H_2{-}CH_2}-)$, 46.61, 48.53 $(-\mathbf{C}\mathrm{(CH_3)(CH_2}-))$, 63.57–69.84 $(-\mathrm{C}{-}\mathbf{C}\mathrm{H_2{-}O}-)$, 88.95, 128.05, 130.63, 142.18, 146.18, 152.00 $(-\mathrm{C}{=}\mathbf{C}{-}\mathrm{C}{=},\ -\mathrm{NH}{-}\mathbf{CH}{=}\mathrm{CH}-)$, 172.48, 173.90 $(-\mathrm{C}{=}\mathrm{O})$ ppm [33].

FTIR spectra were registered on a TENSOR 37 spectrophotometer in the spectral range of 600–4000 cm^{-1}. ^{1}H NMR spectra were registered on a Varian VXR-400 MHz instrument using DMSO-d_6 as a solvent.

The mass loss and the onset temperature of thermo-oxidative destruction T_d were determined in air using a Q50 instrument (TA Instruments, United States) in the temperature range from room temperature to 700°C. The heating rate was 20 K/min. The thermal characteristics were determined in air on a Q2000 apparatus in the temperature range of 90–200°C at a heating rate of 20 K/min.

The ionic conductivity σ_dc of the oligomeric ionic liquids were determined by dielectric relaxation spectroscopy at 40–120°C using a dielectric spectrometer based on a P5083 ac bridge equipped with a stainless steel two-electrode cell. The frequency range of measurements was 0.1–100 kHz. Before testing, the samples were heated to 100°C for 30 min in a flow of dry nitrogen to remove air-sorbed moisture. The measurements were performed in the flow of dry nitrogen.

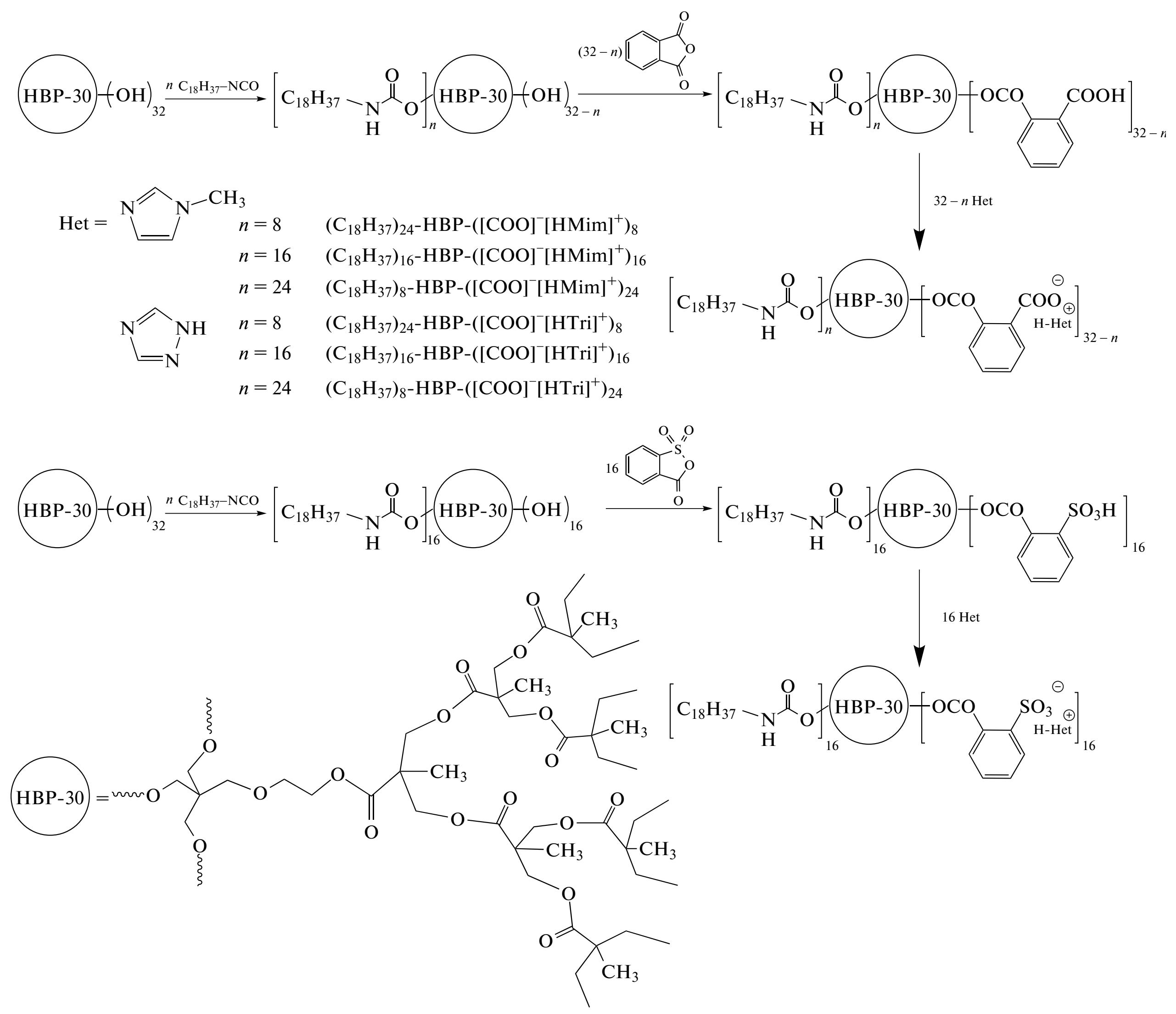
The molecular-weight characteristics of several synthesized compounds were studied by GPC using a Waters Breeze 1515 system chromatograph. Studies were performed using two series-connected Waters Styragel HR 3 THF columns with an internal diameter of 4.6 mm and a length of 300 mm. The columns were packed with a polystyrene gel with an average particle size of 5 μm. Measurements were carried out at 35°C at an eluent flow rate of 0.3 mL/min using 0.25% oligomer solution in THF (75 μL).

RESULTS AND DISCUSSION

The first representatives of the protic oligomeric hyperbranched ionic liquids of the anionic type were synthesized by the exhaustive acylation of the hyperbranched polyesterpolyol containing 32 hydroxyl groups by anhydrides of phthalic or 2-sulfobenzoic acid followed by the neutralization of acidic groups by *N*-methylimidazole [14]. In these compounds, amphiphilicity was determined only by the hydrophobicity of the polyester nucleus and hydrophilicity was imparted by introducing two types of ionic-liquid groups. With this approach, the hydrophobicity was constant for the synthesized series of the hyperbranched ionic liquids and the hydrophilicity was varied only through a change in the nature of anion, namely, carboxylate or sulfonate anions, at the constant nature of cation—*N*-methylimidazolium.

In the present work, the amphiphilicity of the protic hyperbranched ionic liquids was regulated, on one hand, by strengthening of the hydrophobicity of the polyester nucleus via its covalent binding to long-chain alkyl urethane fragments. On the other hand, the hydrophilicity of the ionic-liquid group was varied via a change in the chemical nature of both anion and cation. In addition, the hydrophilic-hydrophobic balance was also controlled by a change in the ratio of the mentioned constituents. As in [14], the aliphatic hyperbranched polyesterpolyol of the third generation containing 32 terminal hydroxyl groups in the shell (HBP-OH) was used as an initial hyperbranched oligomer during the synthesis of ionic hyperbranched liquids [31].

At the first stage, the carbamoylation of the initial HBP-OH of *n*-octadecyl isocyanate at ratios of NCO : OH groups of 8, 16, and 24 was carried out. At the second stage, the acylation of unreacted hydroxyl groups by phthalic anhydride at ratios of $\mathrm{(CO)_2O}$: OH groups of 24, 16, and 8, respectively, was performed. The sulfonic derivatives of the hyperbranched ionic liquids were synthesized according to a similar technique using 2-sulfobenzoic anhydride at a ratio of $\mathrm{(SO_2CO)O}$: OH groups of 16. At the third stage, the formed COOH and $\mathrm{SO_3H}$ groups, respectively, were neutralized by the equivalent amount of *N*-methylimidazole or 1,2,4-1H-triazole. The synthesis schemes of the protic anionic carboxylate and sulfonate ionic liquids of the hyperbranched structure are presented below:



The introduced amounts of *n*-octadecyl urethane fragments and ionic-liquid groups in the hyperbranched ionic liquids are given in the notation of the corresponding compounds. It should be noted that the content of the mentioned hydrophobic and hydrophilic fragments reflects their average distribution.

The synthesized compounds are viscous liquids at room temperature, except the hyperbranched ionic liquids with the highest content of *n*-octadecyl urethane fragments (16 and 24 regardless of the nature of the ionic-liquid group), which are solids with a temperature of transition to the liquid state of 50–65°C. These hyperbranched ionic liquids are well soluble in DMF, DMSO, and chloroform and are insoluble in acetonitrile. With a rise in the content of the hydrophobic fragments, the solubility of the hyperbranched ionic liquids in polar solvents decreases.

The molecular weight of the hyperbranched ionic liquids was calculated from the content of terminal carboxyl or sulfonic acidic groups. A good correlation was observed between the experimental data and the values calculated from the MM of the corresponding hyperbranched carboxylic or sulfonic acids and the MM of heterocycles (Table 1). For $(H_{37}C_{18})_{24}$–HBP–$([COO]^{-}[HMim]^{+})_8$ and $(H_{37}C_{18})_{24}$–HBP–$([COO]^{-}[HTri]^{+})_8$ compounds, which show good solubility in THF, the molecular weight was determined by GPC. The measurement data were as follows: for the first compound, $M_w = 12\,033$ and $M_w/M_n = 1.62$; for the second compound, $M_w = 12\,318$ and $M_w/M_n = 1.59$.

The selection of approaches and modifying compounds for the initial HBP-OH was based on the following prerequisites. The introduction of *n*-octadecyl urethane fragments into the hyperbranched ionic liq-

Table 1. Physicochemical properties of amphiphilic proton hyperbranched oligomeric ionic liquids

No.	Chemical formula	Content of ionic groups, mg-equiv/g	COOH, %		MM_{eq}*		T_d, °C	T_g, °C	T_m, °C	σ_{dc}, S/cm	
			found	calcd.	found	calcd.				at 40°C	at 120°C
1	$HBP–(OH)_{32}$	–	15.4	15.3	3744	3564	–	34	–	–	–
2	$HBP–([COO]^-[HMim]^+)_{32}$	2.93	–	–	10112	10932	145	–16	–	5.60×10^{-6}	6.95×10^{-4}
3	$(C_{18}H_{37})_8–HBP–(COOH)_{24}$	2.27	10.2	11.2	10584	9656	–	–	–	3.00×10^{-11}	5.69×10^{-7}
4	$(H_{37}C_{18})_8–HBP–([COO]^-[HMim]^+)_{24}$	1.91	–	–	12554	11626	173	8.9	–	5.90×10^{-8}	1.90×10^{-4}
5	$(H_{37}C_{18})_8–HBP–([COO]^-[HTri]^+)_{24}$	1.96	–	–	12241	11313	192	5.4	–	7.59×10^{-9}	5.17×10^{-5}
6	$(C_{18}H_{37})_{16}–H_6BP–(COOH)_{16}$	1.44	6.5	6.7	11072	10832	–	–	–	7.15×10^{-11}	1.49×10^{-7}
7	$(H_{37}C_{18})_{16}–HBP–([COO]^-[HMim]^+)_{16}$	1.29	–	–	12386	12146	198	–	51.2	4.10×10^{-9}	1.73×10^{-5}
8	$(H_{37}C_{18})_{16}–HBP–([COO]^-[HTri]^+)_{16}$	1.31	–	–	12177	11937	228	–	47.3	1.90×10^{-8}	3.40×10^{-5}
9	$(C_{18}H_{37})_{24}–HBP–(COOH)_8$	0.62	2.8	3.0	12856	12008	–	–	–	8.00×10^{-11}	3.08×10^{-7}
10	$(H_{37}C_{18})_{24}–HBP–([COO]^-[HMim]^+)_8$	0.59	–	–	13513	12665	263	–	53.0	1.30×10^{-9}	3.70×10^{-6}
11	$(H_{37}C_{18})_{24}–HBP–([COO]^-[HTri]^+)_8$	0.59	–	–	13408	12560	271	–	52.3	1.20×10^{-10}	1.90×10^{-7}
12	$HBP–([SO_3]^-[Hmim]^+)_{32}$**	2.60	–	–	12951	12296	270	–	–	4.04×10^{-4}	3.22×10^{-3}***
13	$(C_{18}H_{37})_{16}–HBP–(SO_3H)_{16}$	1.33	10.8	11.4	12000	11368	–	–	–	1.70×10^{-10}	2.17×10^{-6}
14	$(H_{37}C_{18})_{16}–HBP–([SO_3]^-[HMim]^+)_{16}$	1.20	–	–	13314	12682	294	–	47.0	1.40×10^{-11}	1.62×10^{-5}
15	$(H_{37}C_{18})_{16}–HBP–([SO_3]^-[HTri]^+)_{16}$	1.22	–	–	13105	12473	296	–	51.0	1.20×10^{-11}	5.40×10^{-6}

*MM_{eq} from the content of COOH groups and heterocycles.
**σ_{dc} at 100°C.
***According to [14].

uids promotes the strengthening of intermolecular interaction via the involvement of both alkyl radicals and hydrogen bonds of urethane groups. As is known, carboxyl and sulfonic groups differ in acidities, and *N*-methylimidazole has a higher basicity than 1,2,4-1H-triazole—the pK_a values of the conjugated acids of these compounds are 7.0 [34] and 2.27 [35], respectively. A more complete transition of protons from acid to base was observed in the case of the combination of stronger acids and bases [36]. In other words, the formed ionic-liquid groups possess difference degrees of ionicity. For both series of ionic-liquid groups, the degree of ionicity is higher for the sulfonate and imidazole derivatives.

The IR spectra of the hyperbranched ionic liquids are similar. They show absorption bands due to the stretching vibrations of C–H bonds of CH_2 and CH_3 groups (2770–3041 cm^{-1}), aromatic nuclei (benzene and heterocycles) (3026–3200 cm^{-1}), and C–C bonds of the benzene nucleus (1492–1655 cm^{-1}), which are overlapped by the absorption bands of the bending symmetric and asymmetric vibrations of C–H bonds of CH_2 and CH_3 groups (1371–1377, 1468–1470 cm^{-1}),

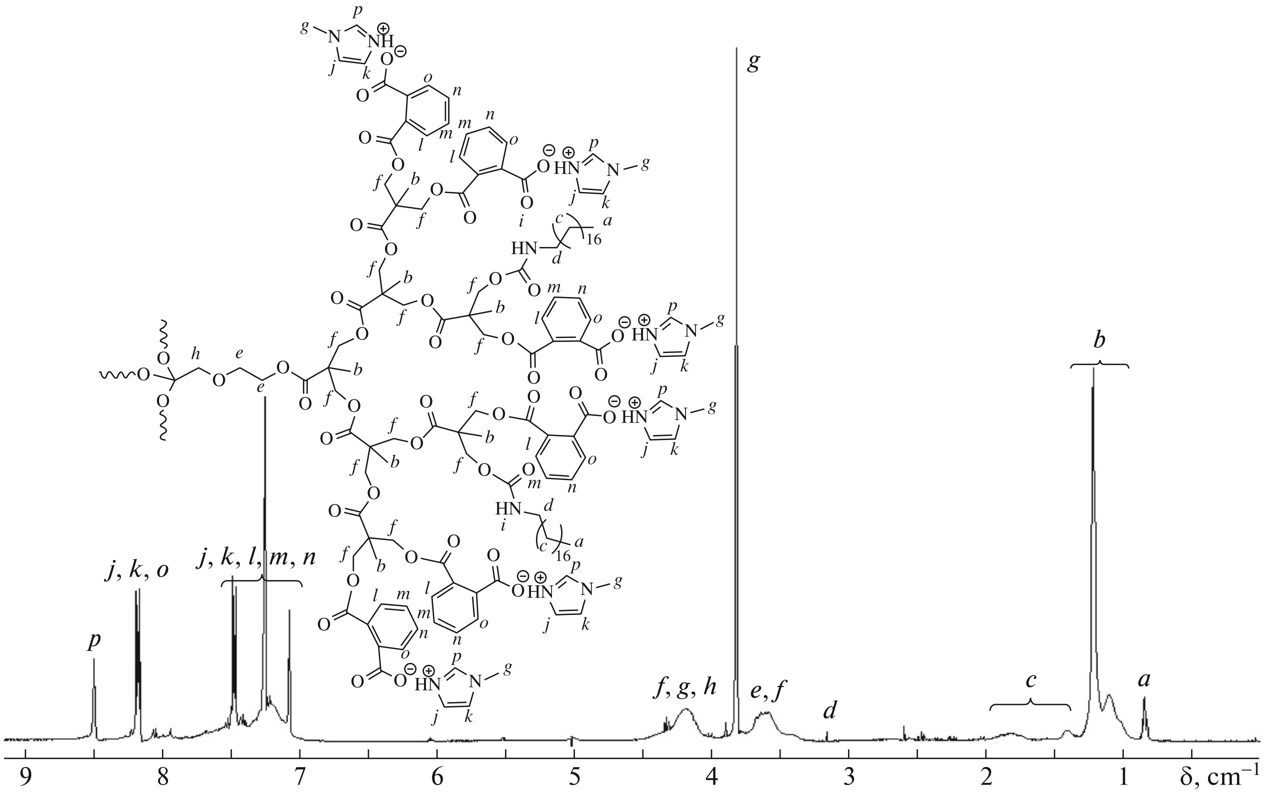


Fig. 1. ^{1}H NMR spectrum of $(C_{18}H_{37})_8$–HBP–$([COO]^-[HMim]^+)_{24}$ (Table 1, compound 4).

the stretching vibrations of C–O–C bonds and C–O bonds of carboxylate groups (1026–1350 cm^{-1}) and S=O sulfonic (1019 cm^{-1}) and C=O bonds of ester and carboxyl groups (1640–1830 cm^{-1}), the overtones of N–H bonds of heterocycles (1825–2200 cm^{-1}), and the absorption band of N–H$^+$ bonds (2300–2700 cm^{-1}) [33].

The ^{1}H NMR spectra of the synthesized compounds are also similar. The typical ^{1}H NMR spectrum for these hyperbranched ionic liquids is given in Fig. 1 using $(C_{18}H_{37})_8$–HBP–$([COO]^-[HMim]^+)_{24}$ compound as an example; there are signals due to the protons of CH_3– (0.86 ppm (*a*)) and –CH_2– (1.37–1.96 ppm (*c*)) groups of *n*-octadecyl fragments, CH_3– groups at the quaternary carbon (1.01–1.37 ppm (*b*)), –CH_2– groups at the α position to nitrogen atoms of the urethane fragments (2.61 ppm (*d*)), –CH_2– groups at the α position to oxygen atoms of olygoester nucleus (3.38–3.74 ppm (*e*, *h*)), protons of N–CH_3 groups of the methylimidazole cation (3.82 ppm (*g*)), CH_2 groups at the α position to oxygen atoms of ester fragments (3.90–4.51 ppm (*f*)), protons of –NH– groups in urethane fragments (5.01 ppm (*i*)), and protons in aromatic cycles (7.35–7.76 ppm (*j*, *k*, *l*, *m*, *n*) and 8.11–8.27 ppm (*j*, *k*, *o*), 8.50 ppm (*p*)) [33].

The distinctive feature of the ^{1}H NMR spectra of the triazolium oligomeric ionic liquids from the imidazolium ones is that the signals due to protons in –CH_3 groups of the methylimidazolium cation (3.82 ppm) and three signals due to protons of the imidazolium nucleus (7.35–7.76, 8.50 ppm) are absent, while additional peaks due to the triazolium cycle (8.11–8.27 ppm) are present.

The ^{13}C NMR spectra of the synthesized compounds are also similar. The typical ^{13}C NMR spectrum for these hyperbranched ionic liquids for $(C_{18}H_{37})_8$–HBP–$([COO]^-[HMim]^+)_{24}$ is given in Fig. 2. There are signals due to carbons $\mathbf{C}H_3$–CH_2– of octadecyl groups (14.16 ppm (*a*)), $\mathbf{C}H_3$– groups at the quaternary carbon (17.45 ppm (*b*)), –$\mathbf{C}H_2$– groups of octadecyl substituents at CH_3 (22.71 ppm (*c*)), –CH_2– groups of octadecyl substituents (26.83, 29.37, 29.73, 31.95 ppm (*d*)), carbons of N–$\mathbf{C}H_3$ groups of the methylimidazolium cation (35.03 ppm (*e*)), –$\mathbf{C}H_2$– groups at the α position to the urethane group (41.18 ppm (*f*)), quaternary carbon (48.51 ppm (*g*)), carbons of $\mathbf{C}H_2$ groups at the α position to polyester –CH_2–C(O)O– and ester –$\mathbf{CH_2}$–O– groups (65.69–77.38 ppm (*h*, *i*)), carbons of –NH–$\mathbf{C}$H=CH– heterocycles (121.81, 122.37 ppm (*j*, *k*, *l*)), aromatic cycles (128.85, 131.21, 132.44, 133.76, 136.21 ppm (*m*, *n*, *o*, *p*, *q*, *r*), and carbon atoms of carboxyl groups (171.54 ppm (*s*)). The distinctive features of the ^{13}C NMR spectra of the triazolium oligomeric ionic liq-

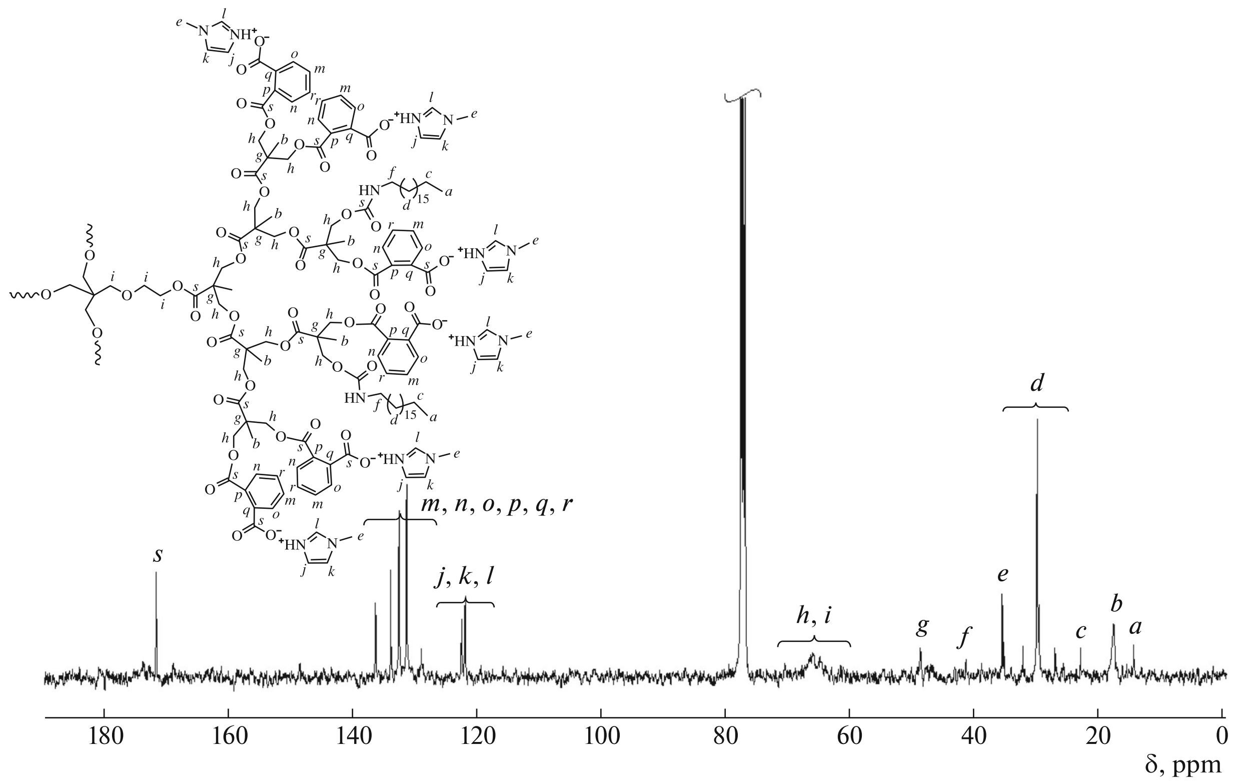


Fig. 2. ^{13}C NMR spectrum of $(C_{18}H_{37})_8$–HBP–([COO]$^-$[HMim]$^+$)$_{24}$ (Table 1, compound 4).

uids from the imidazolium ones are also determined by a change in the heterocyclic counterion.

The results of calorimetry, thermogravimetry, and proton conductivity measurements are presented in the table and Fig. 3. As was found in [14], the protic oligomeric ionic liquids containing only carboxylate and sulfonate-imidazolium groups (HBP–([COO]$^-$[HMim]$^+$)$_{32}$ and HBP–([SO$_3$]$^-$[HMim]$^+$)$_{32}$, respectively) are amorphous compounds. Their glass-transition temperatures T_g are negative; a lower T_g is characteristic of the carboxylate-imidazolium oligomeric ionic liquid. Let us note that the manifestation of glass transition in this type of hyperbranched polymers is connected with the translational motion of a molecule rather than the segmental motion of a chain; despite their high MM, the behavior of such systems is similar to that of oligomers [37, 38].

Upon introduction of the long-chain alkyl urethane fragments into the nucleus, the structural organization changes as follows. $(C_{18}H_{37})_8$–HBP–([COO]$^-$[HMim]$^+$)$_{24}$ and $(C_{18}H_{37})_8$–HBP–([COO]$^-$[HTri]$^+$)$_{24}$ compounds with the minimum content of the *n*-octadecyl urethane fragments among the synthesized substances are also characterized by an amorphous structure (Fig. 3, curves *4*, *5*). In this case, an increase in T_g accompanied by transition to the positive region of temperatures indicates hardening of the system. This effect is more pronounced for the carboxylate-triazolium oligomeric ionic liquid.

The other situation is observed with the rise in the content of *n*-octadecyl urethane fragments in the carboxylic oligomeric ionic liquids to 50% (Fig. 3, compounds 7, 8) and 75% (compounds 10, 11) and in sulfonic ones (compounds 14, 15). There is no glass transition on the temperature dependences of the heat flows of these compounds. This finding may be explained by a fairly high rate of change in heat flow during measurements. At the same time, temperature transitions corresponding to the melting T_m of the crystalline phase of these compounds appear within 47–53°C. The presence of this phase is obviously caused by the tendency of *n*-octadecyl urethane fragments toward formation of crystalline structures. In this case, the values of T_m change depending on both the anion and the cation type. For the carboxylate hyperbranched ionic liquids, the value of T_m is higher for the imidazolium ionic groups, i.e., for the groups with a higher ionicity. However, this difference decreases with the rise in the content of *n*-octadecyl urethane fragments. In the case of sulfonate hyperbranched ionic liquids, the value of T_m is higher for the ionic groups with a lower ionicity of ionic-liquid groups ($(H_{37}C_{18})_{16}$–HBP–([SO$_3$]$^-$[HTri]$^+$)$_{16}$). This is apparently associated with the peculiarities of inter-

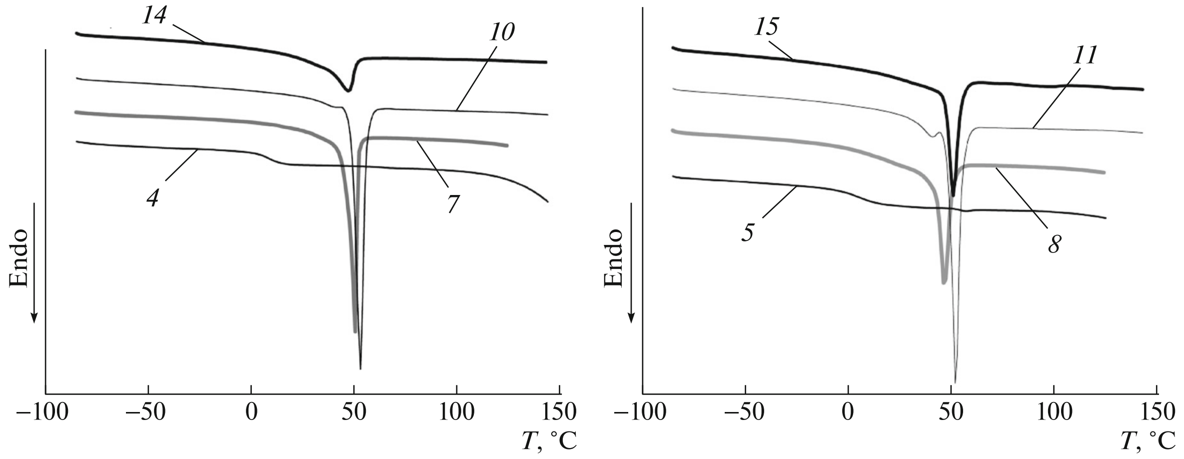


Fig. 3. Temperature dependences of heat flows of anion-active aprotic oligomeric ionic liquids. Here and in Fig. 4, the numbers correspond to the numbers of compounds in table.

molecular interaction between the groups of the mentioned types with a change in the anion type.

The above structural order of the hyperbranched ionic liquids caused by the introduction of *n*-octadecyl urethane fragments also affects the onset temperature of thermo-oxidative destruction T_d corresponding to the 10% mass loss (table). The value of T_d increases with the rise in the content of *n*-octadecyl urethane fragments, achieving a maximum at 271°C for carboxylate hyperbranched ionic liquids and 296°C for sulfonate hyperbranched ionic liquids. The triazolium-containing ionic liquids are more thermostable in the series of carboxylate ionic liquids, i.e., the ionic liquids with a lower ionicity of ionic-liquid groups.

A high ionic conductivity is one of the promising properties of the ionic liquids as nonaqueous ion-conducting media [36, 39]. The proton conductivity σ_{dc} of the hyperbranched ionic liquids under nonaqueous conditions in the temperature range of 40–120°C covering both the solid and liquid states of the crystallizing samples of the hyperbranched ionic liquids was determined (table; Fig. 4). As is seen, an increase in the conductivity of these compounds with increasing temperature provides evidence for their ionic character (Fig. 4) [40].

It is known that conductivity in electrolytes is determined by the amount of charge carriers and their mobility [41]. In its turn, the conductivity of ionic liquids is often reflected in their glass-transition temperature T_g, which is a measure of the cohesion energy of the ionic liquids [36, 39]. Its decrease leads to a fall in T_g. Therefore, it is of interest to consider the influence of structural changes in the synthesized hyperbranched ionic liquids on their proton conductivity. The introduction of *n*-octadecyl urethane fragments into the hyperbranched ionic liquids leading, on one hand, to a decrease in the amount of charge carriers (protons) and, on the other hand, to an increase in T_g entails a decline in proton conductivity relative to that of HBP–$([COO]^-[HMim]^+)_{32}$ and HBP–$([SO_3]^-[Hmim]^+)_{32}$. It is obvious that structuring of the system leads to reduction in the mobility of protons all other conditions being the same. The level of this reduction is determined by the amount of charge carriers in the system.

As a rule, the neutralization of acidic groups by organic bases leads to the rise in the conductivity of ionic liquids [36]. In the case of amorphous and crystalline carboxylate hyperbranched ionic liquids despite the decrease in the concentration of labile protons in them compared with the initial acids, the conductivity grows by approximately two to three orders of magnitude throughout the studied temperature interval, i.e., for both the liquid and solid states (compare the values of σ_{dc} for $(C_{18}H_{37})_8$–HBP–$(COOH)_{24}$, $(C_{18}H_{37})_{16}$–HBP–$(COOH)_{16}$, and $(C_{18}H_{37})_{24}$–HBP–$(COOH)_8$ with those of the neutralized forms) (table). In this case, a higher conductivity is exhibited by the hyperbranched ionic liquids with an increased degree of ionicity of charged groups.

The other situation is observed for the sulfonate hyperbranched ionic liquids, for which the increase in conductivity is observed only at elevated temperatures compared with the acid form (compare the values of σ_{dc} for $(C_{18}H_{37})_{16}$–HBP–$(SO_3H)_{16}$ and its neutralized forms). The effect of the nature of the anionic group on conductivity apparently depends on the aggregate state of the hyperbranched ionic liquids. Moreover, although the degree of ionicity of sulfonate groups is higher, the conductivity of the sulfonate hyperbranched ionic liquids in both the solid and liquid states at equal concentrations of protons is lower than that in the carboxylate analogs $(H_{37}C_{18})_{16}$–HBP–$([COO]^-[HMim]^+)_{16}$ and $(H_{37}C_{18})_{16}$–HBP–$([COO]^-[HTri]^+)_{16}$. In this case, the decisive role is apparently

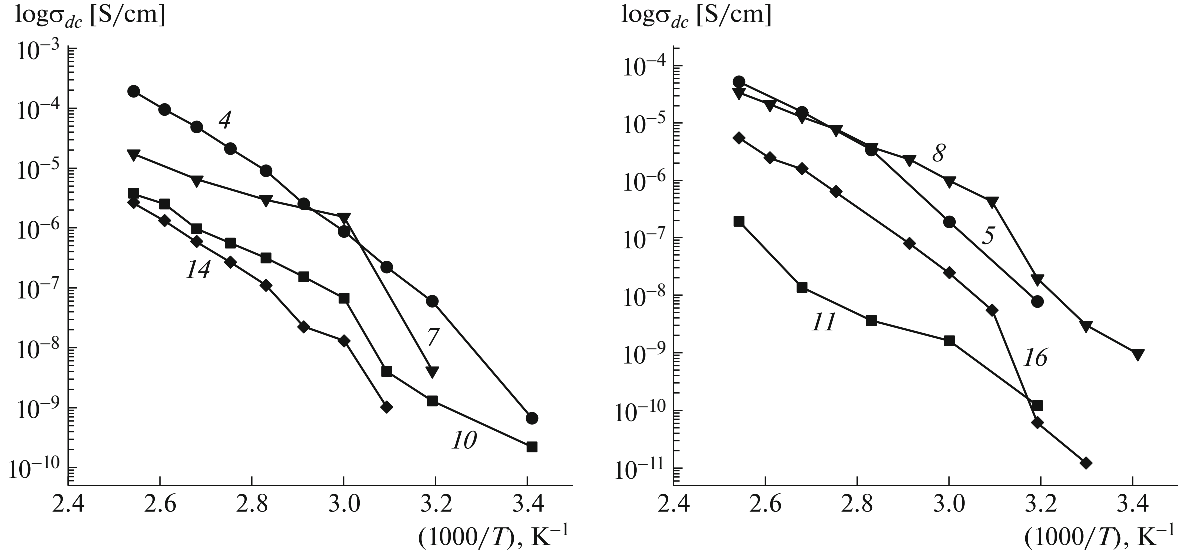


Fig. 4. Temperature dependences of conductivities of oligomeric ionic liquids.

played by other structural factors leading to the ordered packing of heterocycles in the carboxylate hyperbranched ionic liquids followed by implementation of the proton-transfer mechanism in this ordered system inherent for nitrogenous heterocycles [42]. In [14], a higher conductivity of the aprotic imidazolium carboxylate ionic liquids of the linear structure compared with the sulfonate ones was observed throughout the studied temperature range.

As for the cation nature, one should note the following. The conductivity of the amorphous carboxylate ionic liquids of the hyperbranched structure is higher in the case of the imidazolium cation (the average σ_{dc} of the neutralized forms of $(C_{18}H_{37})_8$–HBP–$(COOH)_{24}$), although their T_g are slightly higher. This is probably associated with a higher degree of ionicity of the carboxylate-imidazolium group. In the case of the above-mentioned system structuring caused by the introduction of 16 *n*-octadecyl urethane fragments, a higher conductivity is observed in the case of the triazolium cation. This is apparently caused by its lower T_m. This effect will be considered in more detail below. The further increase in the amount of introduced *n*-octadecyl urethane fragments to 24 accompanied by an approximate equality of T_m for both nitrogenous hyperbranched ionic liquids $(C_{18}H_{37})_{24}$–HBP–$([COO]^-[HMim]^+)_8$ and $(C_{18}H_{37})_{24}$–HBP–$([COO]^-[HTri]^+)_8$ leads to a higher conductivity of the compound with the imidazolium cation. Details of the temperature dependence of proton conductivity make themselves evident in their graphical presentation (Fig. 4). As is seen, the temperature dependences of conductivity for hyperbranched ionic liquids with the maximum content of the ionic-liquid groups (Fig. 4, curves *4*, *5*) are nonlinear in the Arrhenius coordinates. This result indicates that proton transfer in such systems obeys the Grotthuss mechanism [43]. A decrease in the content of ionic-liquid groups in HBP-IL caused by the introduction of *n*-octadecyl urethane fragments leads to the appearance of a conductivity jump on their temperature dependences (Fig. 4). For the imidazolium hyperbranched ionic liquids, the conductivity sharply increases by one to three orders of magnitude as the temperature increases from 40 to 60°C; for the triazolium ones, it increases by one to two orders of magnitude with an increase in temperature from 30 to 60°C. This is caused by the presence of the crystalline phase in the compound that melts at 45–55°C, thereby promoting an increase in proton conductivity (table).

In addition, the conductivity of the hyperbranched ionic liquids regularly grows with an increase in the content of ionic-liquid groups. Note that $(C_{18}H_{37})_{16}$–HBP–$([COO]^-[HMim]^+)_{16}$, despite a lower content of the ionic-liquid groups, is characterized by a higher conductivity compared with $(C_{18}H_{37})_8$–HBP–$([COO]^-[HMim]^+)_{24}$ at 56–69°C. This finding may be apparently attributed to an increase in the mobility of this system after melting of the crystalline phase. In a similar manner, the triazolium hyperbranched ionic liquid $(C_{18}H_{37})_{16}$–HBP–$([COO]^-[HTri]^+)_{16}$ is characterized by a higher conductivity at 40–90°C compared with $(C_{18}H_{37})_8$–HBP–$([COO]^-[HTri]^+)_{24}$. The highest conductivity is exhibited by the hyperbranched ionic liquid $(C_{18}H_{37})_{16}$–HBP–$([COO]^-[HMim]^+)_{16}$, for which the conductivity is 1.9×10^{-4} S/cm at 120°C under nonaqueous conditions.

The self-organization processes of some of the hyperbranched ionic liquids in the aqueous solution and at the interface presented above are described in our work [44].

CONCLUSIONS

The interaction of excess of the hyperbranched polyesterpolyol with 32 terminal hydroxyl groups and *n*-octadecyl isocyanate at different ratios followed by the acylation of hydroxyl groups by phthalic anhydride or 2-sulfobenzoic anhydride and the neutralization of the formed carboxyl or sulfonic groups by *N*-methylimidazole or 1,2,4-1H-triazole resulted in formation of protic amphiphilic hyperbranched anionic ionic liquids with an adjustable ratio of the hydrophilic carboxylate or sulfonate groups and hydrophobic *n*-octadecyl urethane fragments. Depending on content of the latter, the resulting compounds can be liquids at room temperature or form a low-melting crystalline phase. The effect of the degree of ionicity of the ionic-liquid groups on proton conductivity in the range of 40–120°C under nonaqueous conditions is determined by the content of *n*-octadecyl urethane fragments in the hyperbranched ionic liquids. The maximum conductivity is achieved for the carboxy-imidazolium ionic liquid of the hyperbranched structure with the smallest content of alkyl urethane fragments; this value achieves 1.9×10^{-4} S/cm at 120°C. The thermal stability of the hyperbranched ionic liquids in the range of 170–270°C is determined by the nature of the ionic-liquid groups and the amount of introduced alkyl urethane fragments.

The inclination of the hyperbranched ionic liquids to self-organization which is set by different degrees of amphiphilicity in combination with proton conductivity opens prospects for the practical use of these compounds.

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