Electronic Supplementary Information

A Simple and Efficient Synthetic Method for Poly(ethylene terephthalate): Phenylalkyl Pyrrolidinium Ionic Liquid as Polycondensation Medium

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(2a) 1-methyl-1-(3-methylbenzyl)pyrrolidinium bromide [3MBPy][Br] Yield: 85.0 %; T_d: 230 ℃; Found: C, 57.70 %, H, 6.826 %, N, 5.053 %; Calc. for $C_{13}H_{20}NBr$ (270.04): C, 57.77 %, H, 7.41 %, N, 5.18 %; ^{1}H NMR (400 MHz, D_2O): δ = 7.32-7.23 (br, 4H, C_6H_4), 4.36 (s, 2H, $NCH_2C_6H_4$), 3.55-3.48 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.34-3.28 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.85 (s, 3H, NCH_3), 2.28 (s, 3H, $C_6H_4CH_3$), 2.14-2.12 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3021 (m, ν_{Ar-H}), 2997 (m), 2965 (s, ν_{C-H}), 1607 (s), 1588 (s), 1459 (s), 1393 (s), 1164 (m, ν_{C-N}), 905 (s), 877 (s), 809 (s), 747 (s), 700 (s) cm^{-1}.

(2b) 1-methyl-1-(3-methylbenzyl)pyrrolidinium bis(trifluoromethylsulfonyl)-imide [3MBPy][Tf$_2$N] Yield: 90.0 %; Found: C, 38.18 %, H, 4.07 %, N, 5.91 %; Calc. for $C_{15}H_{20}N_2S_2O_4F_6$ (470.08): C, 38.30 %, H, 4.28 %, N, 5.95 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.40-7.34 (br, 4H, C_6H_4), 4.49 (s, 2H, NCH_2Ph), 3.53 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.35 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.88 (s, 3H, NCH_3), 2.37 (s,

3H, PhCH_3), 2.12 (br, 4H, NCH$_2$CH_2CH_2CH$_2$) ppm; IR (KBr pellet): 3058 (w), 2997 (w), 2923 (w), 1612 (m), 1465 (m), 1350 (s, $\nu_{S=O}$), 1337 (s), 1212 (s), 1194 (s, $\nu_{S=O}$), 1138 (s, ν_{C-N}), 1055 (s, ν_{C-F}), 938 (m), 902 (m), 800 (m), 762 (m), 739 (m), 618 (s) cm^{-1}.

(2c) 1-methyl-1-(3-methylbenzyl)pyrrolidinium hexafluorophosphate [3MBPy][PF$_6$] Yield: 84.2 %; Found: C, 46.71 %, H, 5.80 %, N, 4.07 %; Calc. for $C_{13}H_{20}NPF_6$ (334.89): C, 46.58 %, H, 5.97 %, N, 4.18 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.42-7.34 (m, 4H, C$_6H_4$), 4.49 (s, 2H, NCH_2C$_6$H$_4$), 3.54 (m, 2H, NCH_2CH$_2$CH$_2$CH$_2$), 3.44 (m, 2H, NCH$_2$CH$_2$CH$_2$CH_2), 2.88 (s, 3H, NCH_3), 2.37 (s, 3H, PhCH_3), 2.12 (m, 4H, NCH$_2$CH_2CH_2CH$_2$) ppm; IR (KBr pellet): 3035 (w, ν_{Ar-H}), 2994 (w, ν_{C-H}), 1609 (m), 1468 (s), 1425 (m), 1400 (m), 1368 (m), 939 (m), 845 (s), 745 (m), 707 (m), 557 (s) cm^{-1}.

(3a) 1-methyl-1-(4-methylbenzyl)pyrrolidinium bromide [4MBPy][Br] Yield: 88.0 %; T_d: 240 ℃; Found: C, 54.78 %, H, 7.46 %, N, 4.85 %; Calc. for $C_{13}H_{20}NBr$ (269.08): C, 57.78 %, H, 7.46 %, N, 5.18 %; ^{1}H NMR (400 MHz, D$_2$O): δ = 7.34 (d, 2H, C$_6$H$_2H_2$, J = 8.4 Hz), 7.27 (d, 2H, C$_6$H$_2H_2$, J = 8.0 Hz), 4.37 (s, 2H, NCH_2C$_6$H$_4$), 3.53-3.50 (br, 2H, NCH_2CH$_2$CH$_2$CH$_2$), 3.33-3.30 (br, 2H, NCH_2CH$_2$CH$_2$CH$_2$), 2.86 (s, 3H, NCH_3), 2.29 (s, 3H, C$_6$H$_4$CH_3), 2.14-2.13 (br, 4H, NCH$_2$CH_2CH_2CH$_2$) ppm; IR (KBr pellet): 3014 (m, ν_{Ar-H}), 2958 (m, ν_{C-H}), 2891 (m, ν_{C-H}), 1623 (s, ν_{C-C}), 1517 (s), 1456 (s), 1424 (s), 1404 (s), 1381 (m), 1118 (m, ν_{C-N}), 934 (s), 921 (s), 811 (s), 759 (m), 634 (s), 585 (s), 485 (s) cm^{-1}.

(3b) 1-methyl-1-(4-methylbenzyl)pyrrolidinium bis(trifluoromethylsulfonyl)-imide [4MBPy][Tf$_2$N] Yield: 74.0 %; Found: C, 38.26 %, H, 4.26 %, N, 5.74 %; Calc. for $C_{15}H_{20}N_2S_2O_4F_6$ (470.08): C, 38.30 %, H, 4.28 %, N, 5.95 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.44-7.42 (d, 2H, C$_6$H$_2H_2$, J = 8.0 Hz), 7.31-7.29 (d, 2H, C$_6$H$_2H_2$, J = 8.0 Hz), 4.47 (s, 2H, NCH_2Ph), 3.53-3.50 (br, 2H, NCH_2CH$_2$CH$_2$CH$_2$), 3.36-3.32 (br, 2H, NCH_2 CH$_2$CH$_2$CH$_2$), 2.85 (s, 3H, NCH_3), 2.34 (s, 3H, PhCH_3), 2.10-2.09 (br, 4H, NCH$_2$CH_2CH_2CH$_2$) ppm; IR (NaCl): 3033 (m, ν_{Ar-H}), 2982 (m), 2927 (m, ν_{C-H}), 1615 (m), 1517 (m, ν_{C-C}), 1477 (m), 1464 (m), 1429 (w), 1352 (s, $\nu_{S=O}$), 1197 (s, $\nu_{S=O}$), 1138 (s), 1056 (s, ν_{C-F}), 930 (m), 816 (m), 789 (m), 761 (m), 740 (m), 654 (w), 617 (m),

570 (m) cm^{-1}.

(3c) 1-methyl-1-(4-methylbenzyl)pyrrolidinium hexafluorophosphate [4MBPy][PF_6] Yield: 82.0 %; Found: C, 46.34 %, H, 5.77 %, N, 4.09 %; Calc. for $C_{13}H_{20}NPF_6$ (335.12): C, 46.57 %, H, 6.01 %, N, 4.18 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.44-7.42 (d, 2H, $C_6H_2H_2$, J = 8.0 Hz), 7.31-7.29 (d, 2H, $C_6H_2H_2$, J = 8.0 Hz), 4.47 (s, 2H, NCH_2Ph), 3.53-3.50 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.36-3.34 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.85 (s, 3H, NCH_3), 2.34 (s, 3H, $PhCH_3$), 2.09-2.12 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3058 (m, ν_{Ar-H}), 2984 (m), 2923 (m, ν_{C-H}), 1615 (m), 1519 (m, ν_{C-C}), 1480 (m), 1466 (m, ν_{C-H}), 1435 (m), 1395 (m), 833 (s, ν_{P-F}), 558 (s, $\nu_{=C-H}$), 487 (m) cm^{-1}.

(4a) 1-(2-fluorobenzyl)-1-methylpyrrolidinium bromide [2FBPy][Br] Yield: 95.2 %; T_d: 220 ℃; Found: C, 51.85 %, H, 6.76 %, N, 4.93 %; Calc. for $C_{12}H_{17}BrFN$ (273.05): C, 52.57 %, H, 6.25 %, N, 5.11 %; ^{1}H NMR (400 MHz, D_2O): δ = 7.57-7.49 (m, 2H, $C_6H_2H_2$), 7.30-7.23 (m, 2H, $C_6H_2H_2$), 4.54 (s, 2H, $NCH_2C_6H_4$), 3.61-3.55 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.45-3.40 (m, 2H, $NCH_2CH_2CH_2CH_2$), 2.94 (s, 3H, NCH_3), 2.20-2.18 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3008 (m, ν_{Ar-H}), 2966 (m, ν_{C-H}), 1616(s), 1585 (m, ν_{C-C}), 1494 (s), 1469 (m, ν_{C-H}), 1454 (m), 1223 (s, ν_{C-F}), 1191 (m, ν_{C-N}), 1110 (m), 933(m), 917 (m), 782 (s), 769 (s) cm^{-1}.

(4b) 1-(2-fluorobenzyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-imide [2FBPy][Tf_2N] Yield: 79.7 %; Found: C, 35.58 %, H, 3.93 %, N, 5.88 %; Calc. for $C_{14}H_{17}F_7N_2O_4S_2$ (474.05): C, 35.44 %, H, 3.61 %, N, 5.90 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.64-7.58 (m, 2H, $C_6H_2H_2$), 7.41-7.33 (m, 2H, $C_6H_2H_2$), 4.61 (s, 2H, NCH_2Ph), 3.52-3.44 (m, 4H, $NCH_2CH_2CH_2CH_2$), 2.91 (s, 3H, NCH_3), 2.12-2.11 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr): 3039 (w), 3018 (w, ν_{Ar-H}), 2991 (w), 2902 (w, ν_{C-H}), 1618 (m), 1589 (m, ν_{C-C}), 1495 (m), 1480 (m), 1463 (m, ν_{C-H}), 1356 (m, $\nu_{S=O}$), 1189 (s, $\nu_{S=O}$), 1140 (s, ν_{C-F}), 1057 (s), 933 (m), 916 (m), 765 (m), 740 (m), 618 (m), 569 (m), 514 (m) cm^{-1}.

(4c) 1-(2-fluorobenzyl)-1-methylpyrrolidinium hexafluorophosphate [2FBPy][PF_6] Yield: 80.8 %; Found: C, 42.48 %, H, 5.09 %, N, 4.05 %; Calc. for $C_{12}H_{17}F_7NP$ (339.10): C, 42.49 %, H, 5.05 %, N, 4.13 %; ^{1}H NMR (400 MHz,

d-DMSO): δ = 7.64-7.58 (m, 2H, $C_6H_2H_2$), 7.41-7.33 (m, 2H, $C_6H_2H_2$), 4.61 (s, 2H, NCH_2Ph), 3.52-3.43 (m, 4H, $NCH_2CH_2CH_2CH_2$), 2.91 (s, 3H, NCH_3), 2.12-2.11 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3079 (w), 3033 (w, ν_{Ar-H}), 2994 (w), 2914 (w, ν_{C-H}), 1618 (m), 1587 (m, ν_{C-C}), 1495 (m), 1480 (m), 1459 (m, ν_{C-H}), 1236 (m, ν_{C-F}), 1196 (m, ν_{C-N}), 1132 (m), 832 (s, ν_{P-F}), 557 (s) cm^{-1}.

(5a) 1-(3-fluorobenzyl)-1-methylpyrrolidinium bromide [3FBPy][Br] Yield: 93.4 %; T_d: 230 ℃; Found: C, 51.64 %, H, 5.77 %, N, 4.95 %; Calc. for $C_{12}H_{17}BrFN$ (273.05): C, 52.57 %, H, 6.25 %, N, 5.11 %; ^{1}H NMR (400 MHz, D_2O): δ = 7.29-7.02 (m, 4H, C_6H_4), 4.24 (s, 2H, $NCH_2C_6H_4$), 3.37-3.32 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.21-3.15 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.70 (s, 3H, NCH_3), 1.97-1.95 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3028 (m), 3004 (m, ν_{Ar-H}), 2968 (s), 2890 (m, ν_{C-H}), 1616 (m), 1590 (s, ν_{C-C}), 1490 (s), 1454 (s, ν_{C-H}), 1259 (s), 1158 (m, ν_{C-N}), 1146 (m, ν_{C-F}), 900 (m), 876 (m), 804 (m), 759 (m), 696 (m), 521 (m), 452 (m) cm^{-1}.

(5b) 1-(3-fluorobenzyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-imide [3FBPy][Tf$_2$N] Yield: 61.2 %; Found: C, 35.52 %, H, 3.68 %, N, 5.96 %; Calc. for $C_{14}H_{17}F_7N_2O_4S_2$ (474.05): C, 35.44 %, H, 3.61 %, N, 5.90 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.58-7.36 (m, 4H, C_6H_4), 4.54 (s, 2H, NCH_2Ph), 3.56-3.53 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.41-3.37 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.88 (s, 3H, NCH_3), 2.12-2.10 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3067 (w, ν_{Ar-H}), 2978 (w), 2914 (w), 2847 (w, ν_{C-H}), 1618 (w), 1593 (m, ν_{C-C}), 1492 (m), 1452 (m, ν_{C-H}), 1350 (m, $\nu_{S=O}$), 1185 (s, ν_{C-N}), 1132 (s, ν_{C-F}), 1055 (s, ν_{C-F}), 876 (w), 791 (m), 739 (m), 698 (m) cm^{-1}.

(5c) 1-(3-fluorobenzyl)-1-methylpyrrolidinium hexafluorophosphate [3FBPy][PF$_6$] Yield: 49.4 %; Found: C, 42.65 %, H, 5.29 %, N, 4.13 %; Calc. for $C_{12}H_{17}F_7NP$ (339.10): C, 42.49 %, H, 5.05 %, N, 4.13 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.58-7.36 (m, 4H, C_6H_4), 4.54 (s, 2H, NCH_2Ph), 3.56-3.53 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.41-3.37 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.88 (s, 3H, NCH_3), 2.12-2.10 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3097 (w), 3024 (w, ν_{Ar-H}), 2987 (w), 2917 (w), 2847 (w, ν_{C-H}), 1619 (m), 1594 (m, ν_{C-C}), 1492 (m), 1481 (m), 1467 (m), 1452 (m, ν_{C-H}), 1260 (m, ν_{C-F}), 1152 (m, ν_{C-N}), 834 (s, ν_{P-F}), 557 (s,

$\nu_{=C-H}$) cm^{-1}.

(6a) 1-(4-fluorobenzyl)-1-methylpyrrolidinium bromide [4FBPy][Br] Yield: 93.5 %; T_d: 240 ℃; Found: C, 52.52 %, H, 5.87 %, N, 4.96 %; Calc. for $C_{12}H_{17}BrFN$ (273.05): C, 52.57 %, H, 6.25 %, N, 5.11 %; ^{1}H NMR (400 MHz, D_2O): δ = 7.28-7.25 (m, 2H, $C_6H_2H_2$), 6.98-6.93 (m, 2H, $C_6H_2H_2$), 4.19 (s, 2H, $NCH_2C_6H_4$), 3.36-3.27 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.15-3.09 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.65 (s, 3H, NCH_3), 1.93-1.92 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3064 (w), 3001 (m, ν_{Ar-H}), 2972 (m), 2893 (m, ν_{C-H}), 1605 (s), 1510 (s, ν_{C-C}), 1223 (s, ν_{C-F}), 1169 (s, ν_{C-N}), 1018 (s), 828 (s), 781 (m), 615 (m), 538 (m), 505 (m), 424 (m) cm^{-1}.

(6b) 1-(4-fluorobenzyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-imide [4FBPy][Tf_2N] Yield: 86.0 %; Found: C, 35.43 %, H, 3.72 %, N, 5.98 %; Calc. for $C_{14}H_{17}F_7N_2O_4S_2$ (474.05): C, 35.44 %, H, 3.61 %, N, 5.90 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.63-7.60 (m, 2H, $C_6H_2H_2$), 7.36-7.31 (m, 2H, $C_6H_2H_2$), 4.53 (s, 2H, NCH_2Ph), 3.54-3.51 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.38-3.34 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.86 (s, 3H, NCH_3), 2.11-2.10 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (NaCl): 3125 (w), 3079 (w), 3045 (w, ν_{Ar-H}), 2982 (w), 2899 (w, ν_{C-H}), 1609 (m), 1515 (s, ν_{C-C}), 1477 (m), 1465 (m, ν_{C-H}), 1352 (s, $\nu_{S=O}$), 1196 (s, ν_{C-N}), 1138 (s, ν_{Ar-F}), 1056 (s, ν_{C-F}), 842 (m), 789 (m), 653 (w) cm^{-1}.

(6c) 1-(4-fluorobenzyl)-1-methylpyrrolidinium hexafluorophosphate [4FBPy][PF_6] Yield: 67.5 %; Found: C, 42.55 %, H, 5.36 %, N, 4.08 %; Calc. for $C_{12}H_{17}F_7NP$ (339.10): C, 42.49 %, H, 5.05 %, N, 4.13 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.63-7.59 (m, 2H, $C_6H_2H_2$), 7.36-7.32 (m, 2H, $C_6H_2H_2$), 4.52 (s, 2H, NCH_2Ph), 3.51 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.37-3.34 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.86 (s, 3H, NCH_3), 2.11-2.10 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3125 (w), 3089 (w), 3030 (w, ν_{Ar-H}), 2984 (w), 2899 (w, ν_{C-H}), 1608 (m), 1516 (m, ν_{C-C}), 1467 (m, ν_{C-H}), 1232 (m, ν_{C-F}), 1169 (m, ν_{C-N}), 839 (s, ν_{P-F}), 557 (s) cm^{-1}.

(7a) 1-methyl-1-(2-nitrobenzyl)pyrrolidinium bromide [2NBPy][Br] Yield: 97.8 %; T_d: 200 ℃; Found: C, 46.01 %, H, 6.23 %, N, 8.87 %; Calc. for $C_{12}H_{17}BrN_2O_2$ (300.05): C, 47.85 %, H, 5.69 %, N, 9.30 %; ^{1}H NMR (400 MHz, D_2O): δ = 8.16-8.14 (m, 1H, C_6H_3H), 7.78-7.68 (m, 3H, C_6HH_3), 4.94 (s, 2H,

NC*H*$_2$Ph), 3.49-3.47 (br, 4H, NC*H*$_2$CH$_2$CH$_2$C*H*$_2$), 2.90 (s, 3H, NC*H*$_3$), 2.15-2.13 (br, 4H, NCH$_2$C*H*$_2$C*H*$_2$CH$_2$) ppm; IR (KBr pellet): 3032 (m), 3015 (m, ν_{Ar-H}), 1605 (m), 1575 (m, ν_{C-C}), 1527 (s, $\nu_{N=O}$), 1480 (m, ν_{C-H}), 1457 (m), 1348 (s, $\nu_{N=O}$), 1007 (m, ν_{C-N}), 935 (m), 915 (m), 860 (m), 792 (m), 753 (m), 711 (m) cm^{-1}.

(7b) 1-methyl-1-(2-nitrobenzyl)pyrrolidinium bis(trifluoromethylsulfonyl)-imide [2NBPy][Tf$_2$N] Yield: 86.5 %; Found: C, 33.66 %, H, 3.37 %, N, 8.33 %; Calc. for $C_{14}H_{17}F_6N_3O_6S_2$ (501.05): C, 33.53 %, H, 3.42 %, N, 8.38 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 8.16-8.14 (d, 1H, C$_6$H$_3$*H*, *J* = 8.1 Hz), 7.88-7.82 (m, 3H, C$_6$H*H*$_3$), 4.93 (s, 2H, NC*H*$_2$Ph), 3.50 (br, 4H, NC*H*$_2$CH$_2$CH$_2$C*H*$_2$), 2.85 (s, 3H, NC*H*$_3$), 2.09 (br, 4H, NCH$_2$C*H*$_2$C*H*$_2$CH$_2$) ppm; IR (KBr pellet): 3119 (w), 3064 (w), 3034 (w, ν_{Ar-H}), 2981 (w), 2923 (w, ν_{C-H}), 1610 (w), 1580 (w, ν_{C-C}), 1537 (s, $\nu_{N=O}$), 1477 (m), 1455 (m, ν_{C-H}), 1357 (s, $\nu_{S=O}$), 1204 (s, ν_{C-N}), 1142 (s, ν_{Ar-F}), 1059 (s, ν_{C-F}), 929 (m), 907 (m), 861 (m), 833 (m), 798 (m), 762 (m), 741 (m), 705 (m), 622 (s), 611 (s), 569 (s), 514 (s) cm^{-1}.

(7c) 1-methyl-1-(2-nitrobenzyl)pyrrolidinium hexafluorophosphate [2NBPy][PF$_6$] Yield: 85.8 %; Found: C, 39.45 %, H, 4.61 %, N, 7.60 %; Calc. for $C_{12}H_{17}F_6N_2O_2P$ (366.09): C, 39.35 %, H, 4.68 %, N, 7.65 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 8.16-8.14 (d, 1H, C$_6$H$_3$*H*, *J* = 7.8 Hz), 7.88-7.80 (m, 3H, C$_6$H*H*$_3$), 4.93 (s, 2H, NC*H*$_2$Ph), 3.50 (br, 4H, NC*H*$_2$CH$_2$CH$_2$C*H*$_2$), 2.85 (s, 3H, NC*H*$_3$), 2.09-2.08 (br, 4H, NCH$_2$C*H*$_2$C*H*$_2$CH$_2$) ppm; IR (KBr pellet): 3122 (w), 3097 (w), 3070 (w, ν_{Ar-H}), 2978 (w), 2923 (w), 2863 (w, ν_{C-H}), 1610 (m), 1576 (m, ν_{C-C}), 1540 (s, $\nu_{N=O}$), 1478 (m, ν_{C-H}), 1453 (s), 1349 (s, $\nu_{N=O}$), 837 (s, ν_{P-F}), 702 (m), 558 (s) cm^{-1}.

(8a) 1-methyl-1-(3-nitrobenzyl)pyrrolidinium bromide [3NBPy][Br] Yield: 92.8 %; T_d: 240 ℃; Found: C, 47.13 %, H, 5.86 %, N, 9.06 %; Calc. for $C_{12}H_{17}BrN_2O_2$ (300.05): C, 47.85 %, H, 5.69 %, N, 9.30 %; ^{1}H NMR (400 MHz, D$_2$O): δ = 8.36-8.33 (m, 2H, C$_6$H$_2$*H*$_2$), 7.89-7.87 (d, 1H, C$_6$H$_3$*H*, *J* = 8.0 Hz), 7.71-7.67 (t, 1H, C$_6$H$_3$*H*, *J* = 8.0 Hz), 4.58 (s, 2H, NC*H*$_2$Ph), 3.59-3.57 (br, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_2$), 3.43-3.39 (br, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_2$), 2.91 (s, 3H, NC*H*$_3$), 2.21-2.15 (br, 4H, NCH$_2$C*H*$_2$C*H*$_2$CH$_2$) ppm; IR (KBr pellet): 3069 (m), 3003 (m, ν_{Ar-H}), 2960 (m), 2892 (m, ν_{C-H}), 1532 (s, $\nu_{N=O}$), 1474 (m, ν_{C-H}), 1459 (m), 1351 (s, $\nu_{N=O}$), 1090 (m, ν_{C-N}), 878 (m), 902 (m), 819 (m), 808 (m), 747 (m), 723 (m), 699 (m),

675 (m) cm^{-1}.

(8b) 1-methyl-1-(3-nitrobenzyl)pyrrolidinium bis(trifluoromethylsulfonyl)-imide [3NBPy][Tf_2N] Yield: 84.8 %; Found: C, 33.76 %, H, 3.54 %, N, 8.40 %; Calc. for $C_{14}H_{17}F_6N_3O_6S_2$ (501.05): C, 33.53 %, H, 3.42 %, N, 8.38 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 8.48 (s, 1H, C_6H_3H), 8.40-8.38 (d, 1H, C_6H_3H, J = 8.0 Hz), 8.03-8.01 (d, 1H, C_6H_3H, J = 7.5 Hz), 7.83-7.79 (t, 1H, C_6H_3H, J = 7.9 Hz), 4.72 (s, 2H, NCH_2Ph), 3.59-3.57 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.44-3.40 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.92 (s, 3H, NCH_3), 2.14-2.13 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3097 (w), 3080 (w), 3045 (w, ν_{Ar-H}), 2996 (w), 2899 (w, ν_{C-H}), 1619 (w), 1544 (s, $\nu_{N=O}$), 1480 (m), 1464 (m, ν_{C-H}), 1358 (s, $\nu_{S=O}$), 1198 (s, ν_{C-N}), 1139 (s, ν_{Ar-F}), 1049 (s, ν_{C-F}), 810 (m), 791 (m), 741 (m), 703 (m), 675 (m), 615 (s), 570 (s), 514 (s) cm^{-1}.

(8c) 1-methyl-1-(3-nitrobenzyl)pyrrolidinium hexafluorophosphate [3NBPy][PF_6] Yield: 85.3 %; Found: C, 39.51 %, H, 4.53 %, N, 7.51 %; Calc. for $C_{12}H_{17}F_6N_2O_2P$ (366.09): C, 39.35 %, H, 4.68 %, N, 7.65 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 8.48 (s, 1H, C_6H_3H), 8.40-8.38 (d, 1H, C_6H_3H, J = 8.4 Hz), 8.03-8.01 (d, 1H, C_6H_3H, J = 7.5 Hz), 7.83-7.79 (t, 1H, C_6H_3H, J = 8.0 Hz), 4.72 (s, 2H, NCH_2Ph), 3.60-3.57 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.44-3.41 (m, 2H, $NCH_2CH_2CH_2CH_2$), 2.92 (s, 3H, NCH_3), 2.14-2.13 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3102 (w), 3085 (w), 3045 (w), 3021 (w, ν_{Ar-H}), 2986 (w), 2902 (w, ν_{C-H}), 1620 (m), 1584 (w, ν_{C-C}), 1536 (s, $\nu_{N=O}$), 1479 (s), 1453 (m), 1433 (m), 1398 (m, ν_{C-H}), 1348 (s, $\nu_{N=O}$), 1094 (m, ν_{C-N}), 831 (s, ν_{P-F}), 746 (m), 699 (m), 674 (m), 557 (s) cm^{-1}.

(9a) 1-methyl-1-(4-nitrobenzyl)pyrrolidinium bromide [4NBPy][Br] Yield: 94.7 %; T_d: 240 ℃; Found: C, 48.43 %, H, 5.65 %, N, 9.26 %; Calc. for $C_{12}H_{17}BrN_2O_2$ (300.05): C, 47.85 %, H, 5.69 %, N, 9.30 %; ^{1}H NMR (400 MHz, D_2O): δ = 8.31-8.29 (d, 2H, $C_6H_2H_2$, J = 8.5 Hz), 7.76-7.73 (d, 2H, $C_6H_2H_2$, J = 8.5 Hz), 4.60 (s, 2H, NCH_2Ph), 3.62-3.59 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.47-3.42 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.94 (s, 3H, NCH_3), 2.23-2.18 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3038 (m), 3007 (m, ν_{Ar-H}), 2963 (m), 2886 (m, ν_{C-H}), 1605 (s, ν_{C-C}),

1527 (s, $\nu_{N=O}$), 1461 (m, ν_{C-H}), 1346 (s, $\nu_{N=O}$), 1105 (m), 1076 (m), 1013 (m, ν_{C-N}), 881 (m), 857 (m), 838 (m), 722 (m), 703 (m) cm^{-1}.

(9b) 1-methyl-1-(4-nitrobenzyl)pyrrolidinium bis(trifluoromethylsulfonyl)-imide [4NBPy][Tf$_2$N] Yield: 76.0 %; Found: C, 33.79 %, H, 3.86 %, N, 8.37 %; Calc. for $C_{14}H_{17}F_6N_3O_6S_2$ (501.05): C, 33.53 %, H, 3.42 %, N, 8.38 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 8.34-8.32 (d, 2H, $C_6H_2H_2$, J = 8.0 Hz), 7.86-7.84 (m, 2H, $C_6H_2H_2$, J = 8.4 Hz), 4.69 (s, 2H, NCH_2Ph), 3.59-3.56 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.44-3.40 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.90 (s, 3H, NCH_3), 2.13-2.12 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (NaCl): 3119 (w), 3085 (w, ν_{Ar-H}), 2983 (w, ν_{C-H}), 1610 (m, ν_{C-C}), 1529 (s, $\nu_{N=O}$), 1477 (m), 1464 (m, ν_{C-H}), 1352 (s, $\nu_{S=O}$), 1194 (s, ν_{C-N}), 1138 (s, ν_{Ar-F}), 1056 (s, ν_{C-F}), 856 (m), 830 (w), 789 (m), 704 (w), 653 (w) cm^{-1}.

(9c) 1-methyl-1-(4-nitrobenzyl)pyrrolidinium hexafluorophosphate [4NBPy][PF$_6$] Yield: 80.6 %; Found: C, 39.47 %, H, 4.48 %, N, 7.60 %; Calc. for $C_{12}H_{17}F_6N_2O_2P$ (366.09): C, 39.35 %, H, 4.68 %, N, 7.65 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 8.18-8.16 (d, 2H, $C_6H_2H_2$, J = 8.4 Hz), 7.69-7.67 (d, 2H, $C_6H_2H_2$, J = 8.4 Hz), 4.52 (s, 2H, NCH_2Ph), 3.41-3.39 (br, 2H, $NCH_2CH_2CH_2CH_2$), 3.27-3.23 (br, 2H, $NCH_2CH_2CH_2CH_2$), 2.73 (s, 3H, NCH_3), 1.96-1.94 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3119 (m), 3080 (m), 3024 (m, ν_{Ar-H}), 2987 (m), 2957 (m), 2908 (w), 2866 (m, ν_{C-H}), 1601 (s, ν_{C-C}), 1530 (s, $\nu_{N=O}$), 1479 (s), 1467 (s, ν_{C-H}), 1358 (s, $\nu_{N=O}$), 1212 (s), 1192 (m, ν_{C-N}), 848 (s, ν_{P-F}), 557 (s) cm^{-1}.

(10a) 1-methyl-1-(2-phenethyl)pyrrolidinium bromide [PhEPy][Br] Pale yellow solid with easily hydroscopic. T_d: 260 ℃; Found: C, 54.94 %, H, 6.54 %, N, 5.39 %; Calc. for $C_{13}H_{20}BrN$ (269.08): C, 57.78 %, H, 7.46 %, N, 5.18 %; ^{1}H NMR (400 MHz, D_2O): δ = 7.39-7.37 (m, 2H, $C_6H_3H_2$), 7.33-7.32 (m, 3H, $C_6H_2H_3$), 3.58-3.55 (t, 2H, NCH_2CH_2Ph, J = 8.1 Hz), 3.54-3.52 (m, 4H, $NCH_2CH_2CH_2CH_2$), 3.16-3.12 (t, 2H, CH_2Ph, J = 8.8 Hz,), 3.10 (s, 3H, NCH_3), 2.19 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3058 (m), 3021 (m), 3000 (m, ν_{Ar-H}), 2969 (m), 2954 (m), 2887 (m, ν_{C-H}), 1601 (m), 1583 (w, ν_{C-C}), 1456 (s, ν_{C-H}), 1181 (w, ν_{C-N}), 1088 (m), 1045 (m), 1015 (m), 993 (m), 966 (m), 932 (s), 759 (s), 702 (s), 552 (m), 509 (s) cm^{-1}.

(10b) 1-methyl-1-(2-phenethyl)pyrrolidinium bis(trifluoromethylsulfonyl)-

imide [PhEPy][Tf_2N] Yield: 81.7 %; Found: C, 38.34 %, H, 4.10 %, N, 5.92 %; Calc. for $C_{15}H_{20}F_6N_2O_4S_2$ (470.08): C, 38.30 %, H, 4.28 %, N, 5.95 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.34-7.26 (m, 5H, C_6H_5), 3.55 (m, 2H, NCH_2CH_2Ph), 3.51 (br, 4H, $NCH_2CH_2CH_2CH_2$), 3.08 (s, 3H, NCH_3), 3.05-3.03 (m, 2H, CH_2Ph), 2.10 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3094 (w), 3070 (w), 3039 (w, ν_{Ar-H}), 2980 (w), 2939 (w), 2896 (w, ν_{C-H}), 1605 (m), 1529 (s, ν_{C-C}), 1464 (m), 1436 (m), 1344 (s, $\nu_{S=O}$), 1185 (s, ν_{C-N}), 1136 (s, ν_{Ar-F}), 1061 (s, ν_{C-F}), 788 (m), 739 (m), 700 (m), 653 (m), 599 (s), 570 (s), 507 (s) cm^{-1}.

(10c) 1-methyl-1-(2-phenethyl)pyrrolidinium hexafluorophosphate [PhEPy][PF_6] Yield: 61.9 %; Found: C, 46.74 %, H, 5.70 %, N, 3.81 %; Calc. for $C_{13}H_{20}F_6NP$ (335.12): C, 46.57 %, H, 6.01 %, N, 4.18 %; ^{1}H NMR (400 MHz, d-DMSO): δ = 7.13-7.02 (m, 5H, C_6H_5), 3.31 (m, 2H, NCH_2CH_2Ph), 3.27 (br, 4H, $NCH_2CH_2CH_2CH_2$), 2.84 (s, 3H, NCH_3), 2.82-2.80 (m, 2H, CH_2Ph), 1.86 (br, 4H, $NCH_2CH_2CH_2CH_2$) ppm; IR (KBr pellet): 3076 (w), 3033 (w, ν_{Ar-H}), 2983 (w), 2941 (w, ν_{C-H}), 1605 (w, ν_{C-C}), 1468 (m), 1431 (w, ν_{C-H}), 1403 (w), 837 (s, ν_{P-F}), 755 (m), 701 (m), 557 (s) cm^{-1}.

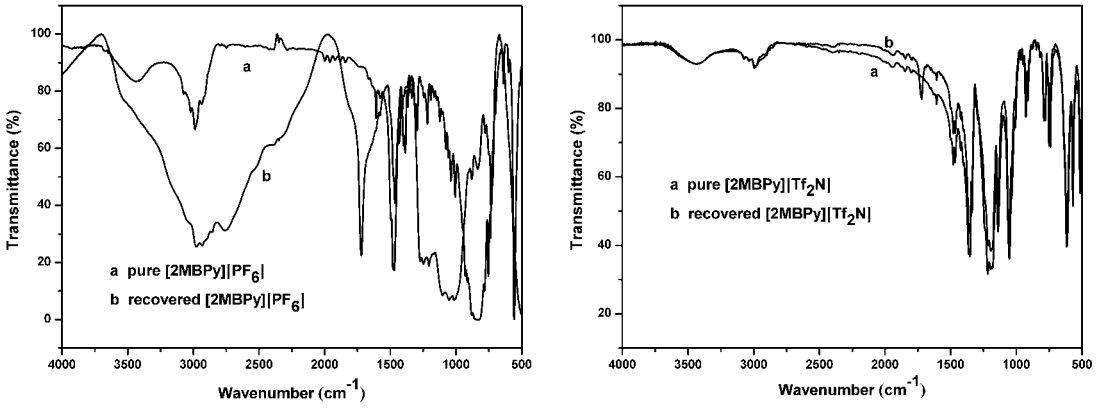

Fig. S1. The FTIR spectra of the pure ILs (a) and the recovered ILs (b).

Fig. S2. Photographs of the polycondensation of BHET in [4FBPy][PF_6] (A-D) and [2FBPy][Tf_2N] (E-H) using Sb_2O_3 as catalyst.

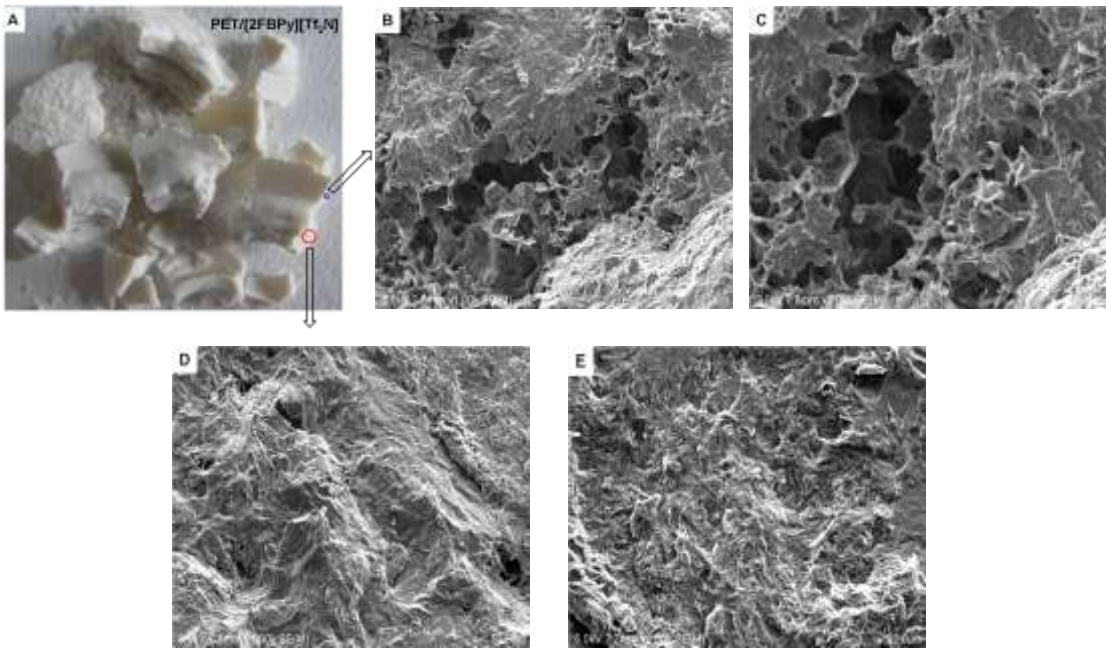

Fig. S3. SEM images of the fractured surface of PET/[2FBPy][Tf_2N] at different area: at edge (B, C) and center (D, E). PET/[2FBPy][Tf_2N] prepared by polycondensation of BHET in [2FBPy][Tf_2N] using Sb_2O_3 as catalyst.

Table S1 The physical properties of phenylalkyl pyrrolidinium ILs

Ionic liquid	State	T_m (℃)	T_d (℃)	Ionic liquid	State	T_m (℃)	T_d (℃)
[2MBPy][PF_6]	White powder	140	320	[2MBPy][Tf_2N]	White powder	79	340
[3MBPy][PF_6]	White powder	61	330	[3MBPy][Tf_2N]	White powder	35	350
[4MBPy][PF_6]	White powder	116	320	[4MBPy][Tf_2N]	Colorless liquid	-52[a]	360
[2FBPy][PF_6]	White solid	197	340	[2FBPy][Tf_2N]	White solid	51	380
[3FBPy][PF_6]	White powder	97	320	[3FBPy][Tf_2N]	White solid	40	390
[4FBPy][PF_6]	White powder	121	320	[4FBPy][Tf_2N]	Colorless liquid	-58[a]	360
[2NBPy][PF_6]	White powder	179	290	[2NBPy][Tf_2N]	Grey white solid	40	310
[3NBPy][PF_6]	White powder	190	310	[3NBPy][Tf_2N]	White powder	67	340
[4NBPy][PF_6]	White powder	150	300	[4NBPy][Tf_2N]	Yellow solid	50	320
[PhEPy][PF_6]	White powder	213	330	[PhEPy][Tf_2N]	White powder	52	400

[a] Glass transition temperature at the midpoint.

Table S2. Polycondensation of BHET with different amounts of ILs [a]

Entry	IL	Catalyst	IL (wt%)	$M_w/10^4$ (g mol^{-1})	PDI	Yield (%)
1	[4FBPy][Tf_2N]	$Sb(OAc)_3$	80	2.34	1.51	88.0
2	[4FBPy][Tf_2N]	$Sb(OAc)_3$	50	1.90	2.09	73.0
3	[4FBPy][Tf_2N]	$Sb(OAc)_3$	30	1.52	2.57	85.0
4	[4FBPy][Tf_2N]	$Sb(OAc)_3$	20	1.15	2.30	84.0
5	[4FBPy][Tf_2N]	$Sb(OAc)_3$	5	0.76	2.22	77.9

[a] Polymerization conditions, see footnotes of Table 1.

Table S3. Polycondensation of BHET at different temperatures [a]

Entry	IL	Catalyst	Temperature (℃)	$M_w/10^4$ (g mol^{-1})	PDI	Yield (%)
1	[4MBPy][Tf_2N]	EGSb	240	1.03	1.53	84.7
2	[4MBPy][Tf_2N]	EGSb	230	1.40	2.07	78.8
3	[4MBPy][Tf_2N]	EGSb	220	1.10[b]	1.30	85.0
4	[4MBPy][Tf_2N]	EGSb	210	0.72[b]	1.73	68.0
5	[4MBPy][Tf_2N]	EGSb	200	0.60[b]	1.19	65.0
6	[4MBPy][Tf_2N]	EGSb	190	0.31[b]	1.58	65.0

[a] Polymerization conditions, see footnotes of Table 1. [b] Bimodal distribution.

Table S4. Water content of the samples [a]

Sample	IL[b]	IL[c]	BHET	EGSb	$Sb(OAc)_3$	Mixture[d]	Mixture[e]
H_2O /wt%	0.0282	0.0467	0.4363	1.3195	5.1850	0.4019	0.3559

[a] Samples are dried at 60 ℃ under vacuum. [b] [3MBPy][PF_6]. [c] [3MBPy][Tf_2N]. [d] PET/[3MBPy][Tf_2N] prepared by polycondensation of BHET in [3MBPy][Tf_2N] using EGSb as catalyst. e PET/[3MBPy][Tf_2N] prepared by polycondensation of BHET in [3MBPy][Tf_2N] using $Sb(OAc)_3$ as catalyst.