Supporting information

A Facile Route to Realize the Copolymerization of L-Lactic Acid and ε-Caprolactone: Sulfonic Acid-functionalized Brønsted Acidic Ionic Liquids as both solvents and catalysts

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[BSMIM][TFS] Anal. Calc. for $C_9H_{15}F_3N_2O_6S_2$: C, 29.35, H, 4.10, N, 7.61; Found: C, 28.58, H, 5.552, N,7.308. ^{1}H NMR (400 MHz, DMSO) δ 9.13 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 4.18 (t, J = 7.0 Hz, 2H), 3.85 (s, 3H), 2.53 (2H), 1.98 – 1.75 (m, 2H), 1.65 – 1.41 (m, 2H). ^{13}C NMR (400 MHz, DMSO) δ 135.93 (s), 123.36 (s), 122.00 (s), 121.70 (s), 118.51 (s), 50.03 (s), 48.48 (s), 35.53 (s), 28.09 (s), 21.07 (s).

[BSMIM][HSO_4] Anal. Calc. for $C_8H_{16}N_2O_7S_2$: C, 30.37; H, 5.10; N, 8.86; Found: C, 29.23, H, 7.018, N, 8.368. ^{1}H NMR (400 MHz, DMSO) δ 9.14 (s, 1H), 7.77 (s, 1H), 7.71 (s, 1H), 5.99 (s, 7H), 4.18 (t, J = 6.8 Hz, 2H), 3.85 (s, 3H), 2.48 (2H), 1.98 – 1.75 (m, 2H), 1.55 (dd, J = 14.5, 7.3 Hz, 2H). ^{13}C NMR (400 MHz, DMSO) δ 135.81 (s), 123.34 (s), 121.95 (s), 49.98 (s), 48.47 (s), 35.51 (s), 28.00 (s), 20.96 (s).

[BSMIM][TS] Anal. Calc. for $C_{15}H_{22}N_2O_6S_2$: C, 41.59, H, 6.906, N, 6.294; Found: C, 46.14, H, 5.68, N, 7.17^{1}H NMR (400 MHz, DMSO) δ 9.14 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 7.48 (d, J = 7.4 Hz, 2H), 7.12 (d, J = 7.5 Hz, 2H), 5.85 (s, 4H), 4.18 (t, J = 6.4 Hz, 2H), 3.85 (s, 3H), 2.44 (2H), 2.29 (s, 3H), 1.98 – 1.75 (m, 2H), 1.55 (d, J = 6.8 Hz, 2H). ^{13}C NMR (400 MHz, DMSO) δ 142.65 (s), 139.61 (s), 135.80 (s), 128.56 (s), 125.26 (s), 123.33 (s), 121.95 (s), 50.00 (s), 48.47 (s), 35.51 (s), 28.04 (s), 21.00 (s), 20.55 (s).

[BSMIM][MS] Anal. Calc. for $C_9H_{18}N_2O_6S_2$: C, 34.38; H, 5.77; N, 8.91; Found: C, 33.91, H, 5.009, N, 8.767. ^{1}H NMR (400 MHz, DMSO) δ 9.14 (s, 1H), 7.77 (s, 1H), 7.71 (s, 1H), 4.18 (t, J = 6.9 Hz, 2H), 3.85 (s, 3H), 2.46 (2H), 2.39 (s, 3H), 1.98 – 1.75 (m, 2H), 1.54 (dt, J = 14.8, 7.5 Hz, 2H). ^{13}C NMR (400 MHz, DMSO) δ 135.94 (s), 123.38 (s), 122.01 (s), 50.04 (s), 48.47 (s), 39.13 (s), 37.90 (s), 35.55 (s), 28.10 (s), 21.07 (s).

[BSMIM][BF_4]Anal. Calc. for $C_8H_{15}BF_4N_2O_3S$: C, 31.39, H, 4.94, N, 9.15; Found: C, 32.09, H, 5.950, N, 9.303. ^{1}H NMR (400 MHz, DMSO) δ 9.13 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 4.18 (t, J = 6.9 Hz, 2H), 3.85 (s, 3H), 2.46 (2H), 1.98 – 1.75 (m, 2H), 1.65 – 1.41 (m, 2H). ^{13}C NMR (400 MHz, DMSO) δ 135.93 (s), 123.35 (s), 121.99 (s), 50.04 (s), 48.47 (s), 35.52 (s), 28.08 (s), 21.07 (s).

[BSPy][HSO_4] ^{1}H NMR (400 MHz, DMSO) δ 9.10 (d, J = 5.5 Hz, 2H), 8.61 (t, J = 7.8 Hz, 1H), 8.17 (t, J = 7.8 Hz, 2H), 4.63 (t, J = 7.3 Hz, 2H), 2.10 – 1.94 (m, 2H), 1.64 – 1.52 (m, 2H).

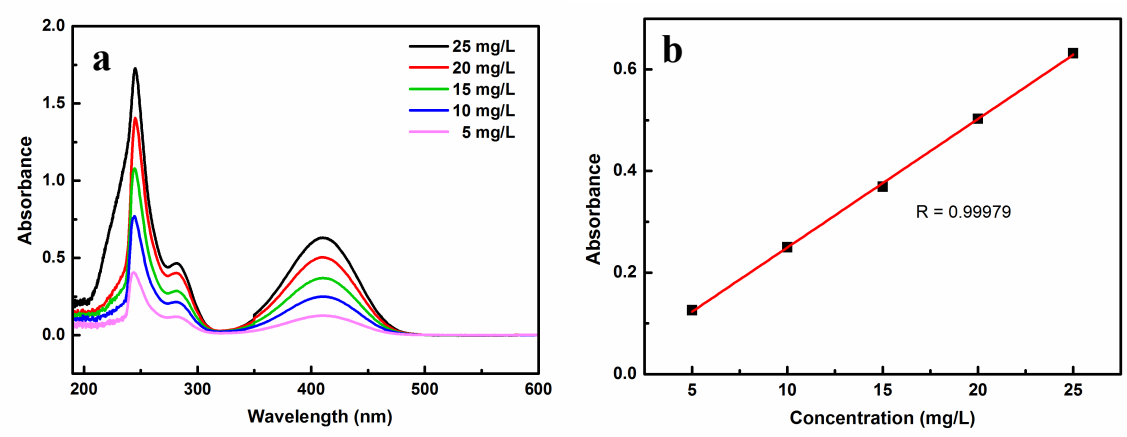


Fig. S1 (a) UV-Vis spectra of 2,4-dichloro-6-nitroaniline chloroform solutions with different concentration; (b)The intensities based on the absorption maximum from each curve in the UV-Vis spectra for the different concentration of 2,4-dichloro-6-nitroaniline chloroform solution.

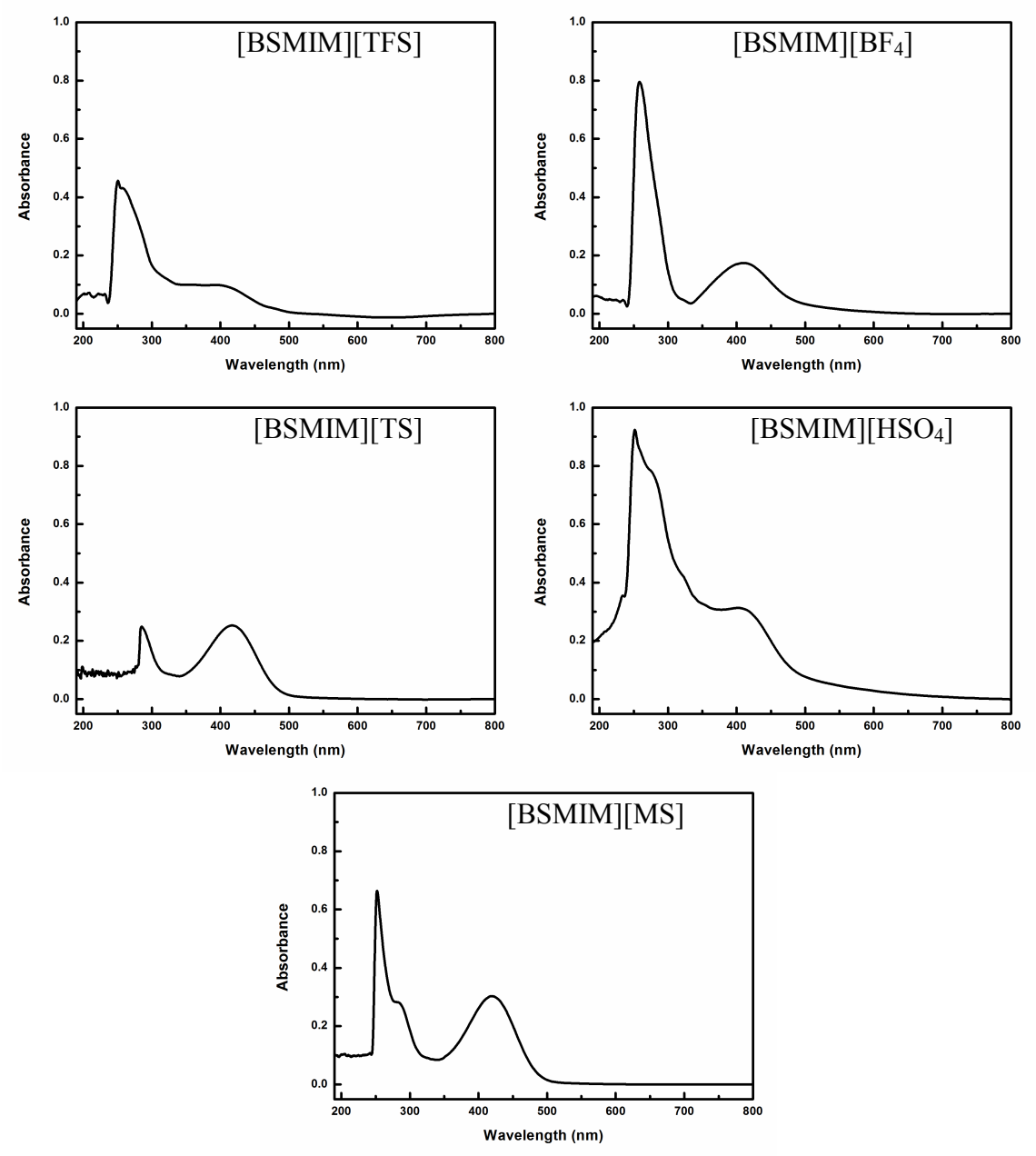
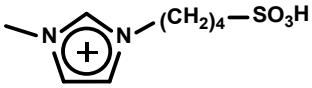


Fig. S2 UV-Vis spectra of 2,4-dichloro-6-nitroaniline in different sulfonic acid-functionalized Brønstedacidic ionic liquids (50 °C, 25 mg/L).

Table S1 H_0 values of SFBAILs determined by UV-Vis spectroscopy at 50 °C.

SFBAILs	Cations	Anions	[I]%	[IH^+]%	H_0[a]
[BSMIM][TFS]		$CF_3SO_3^-$	14	86	-4.1
[BSMIM][BF_4]		BF_4^-	28	72	-3.7
[BSMIM][TS]		*p*-$CH_3(C_6H_4)SO_3^-$	41	59	-3.5
[BSMIM][HSO_4]		HSO_4^-	48	52	-3.3
[BSMIM][MS]		$CH_3SO_3^-$	48	52	-3.3

[a] The acidities of SFBAILs were determined usingthe Hammett method with UV-Vis spectroscopy at 50 °C, 25 mg/L of 2,4-dicholoro-6-nitroaniline as indicator.

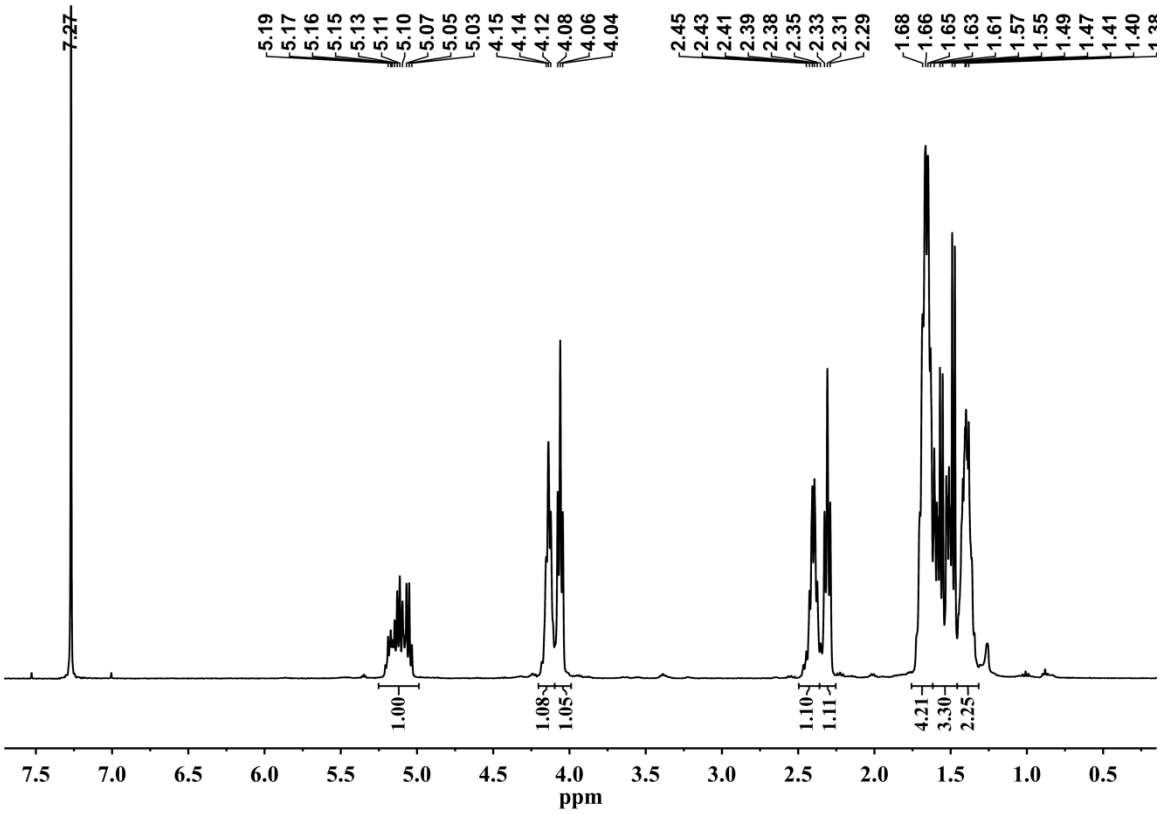


Fig. S3 ^{1}H NMR spectrum of PLLA-CL copolymer by blowing dry air (with an initial monomer ratio of 1:1).

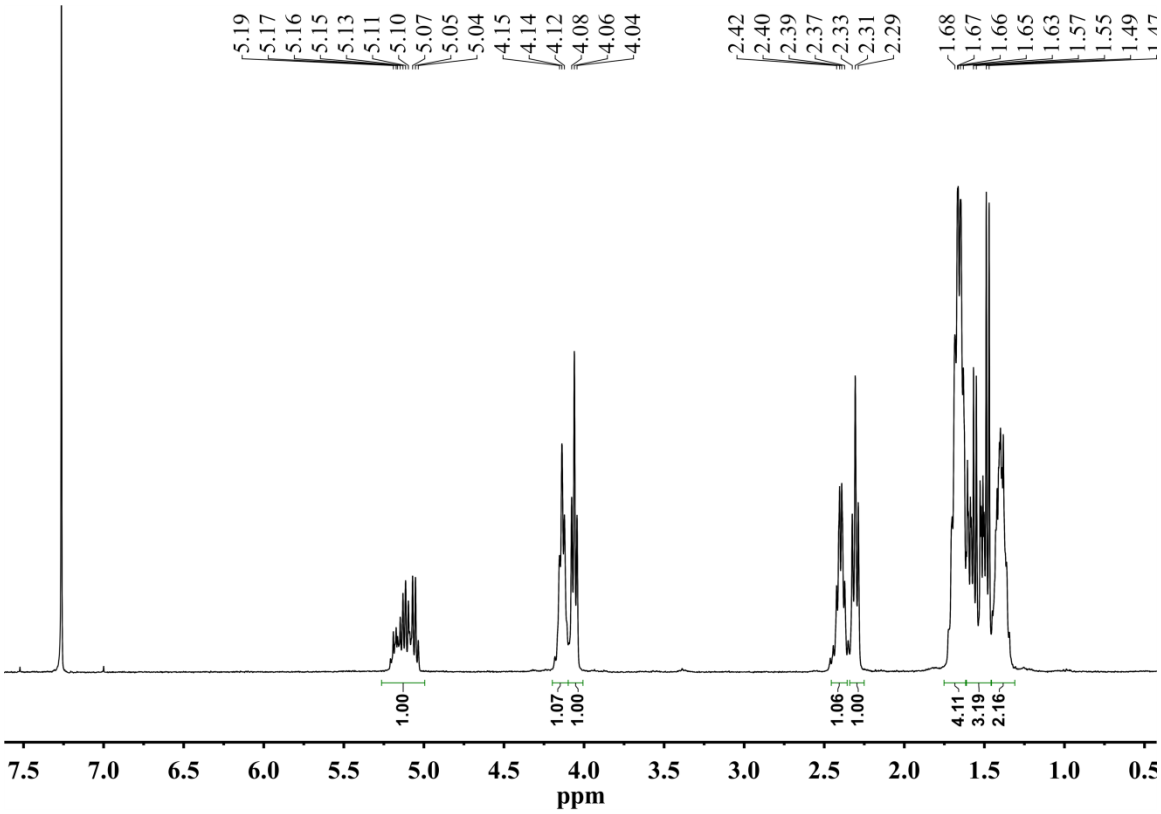


Fig. S4 ^{1}H NMR spectrum of PLLA-CL copolymer (with an initial monomer ratio of 1:1).

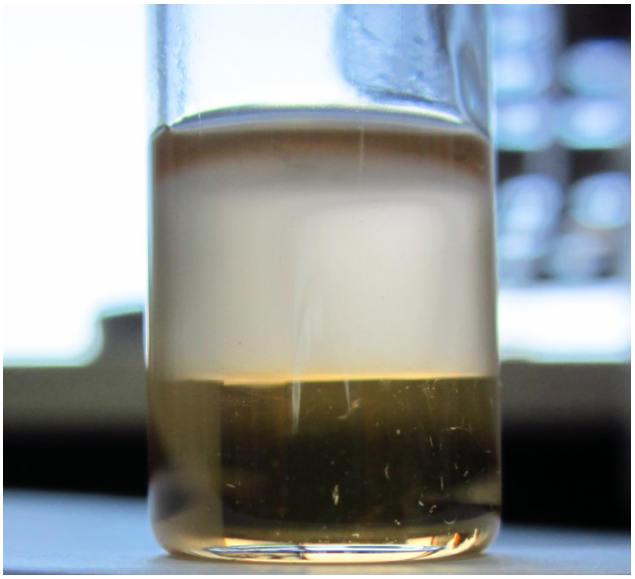


Fig. S5 Digital photo image of polymerization mixture after phase separation (upper phase for PLLA-CL copolymer, lower phase for [BSMIM][TFS]).

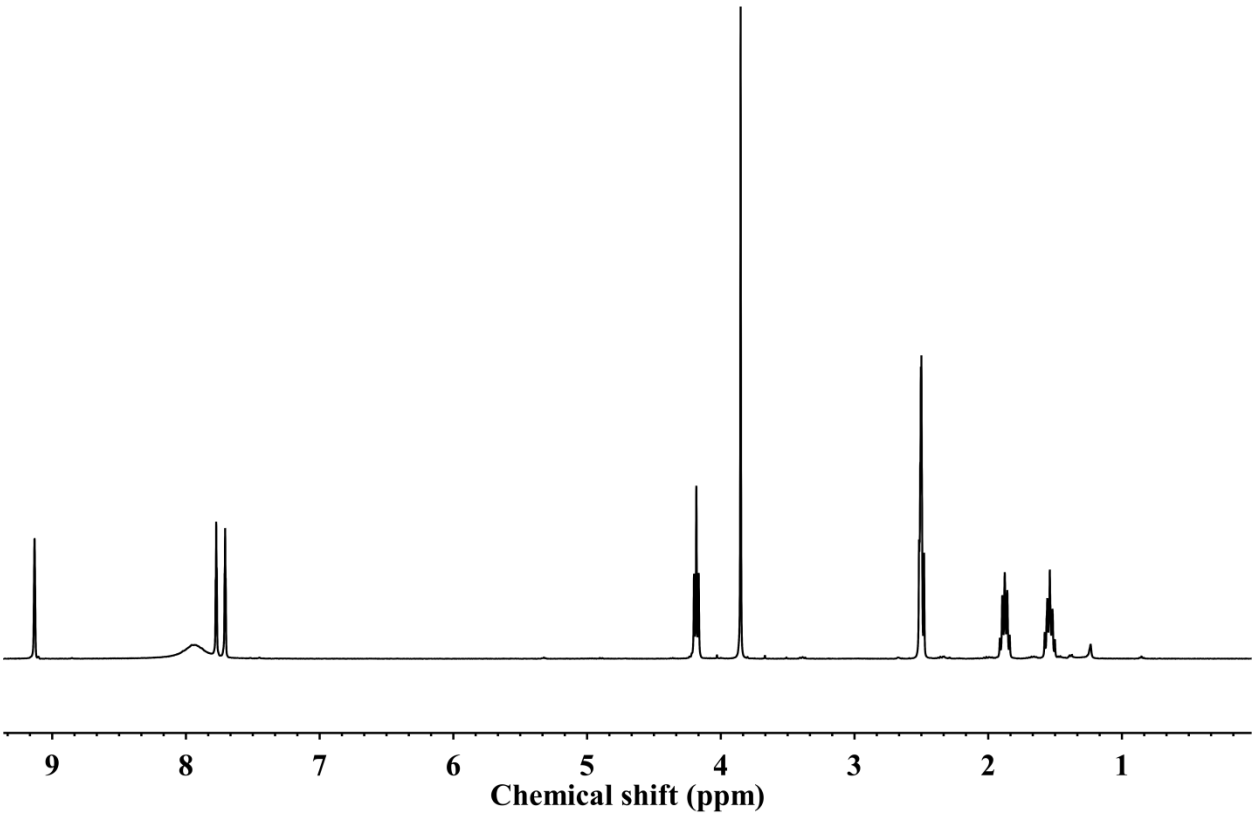


Fig. S6 ^{1}H NMR spectrum of recycled [BSMIM][TFS].