Electronic Supplementary Information

LCST-type polymers based on Chiral-Polymeric Ionic Liquids

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CPIls Synthesis

Scheme S.I.1 Synthesis of CPIl polymers

Preparation of compound 2. Poly(vinylbenzyl chloride) (2) was prepared by bulk RAFT polymerization of p-chloromethylstyrene (1) with IBN as chain transfer agent and AIBN as initiator. A flask was charged with 0.1459 g (0.66 mmol) of IBN, 10.0079 g (65.57 mmol) of compound 1 and 0.0108 g (0.065 mmol) of AIBN. The flask was deoxygenated with five freeze-thaw-cycles and filled with nitrogen. The polymerization was allowed to proceed at 120 °C for 24 hours. The reaction was stopped by immersing the flask into liquid nitrogen. The product was diluted with acetone and isolated by precipitation with methanol. The product was further purified by two precipitations from acetone/methanol to yield Poly(VBC) 2 with a 56 % polymerization degree, a molecular weight of 18.9 kg/mol and a polydispersity of 1.5 as determined by GPC.

Preparation of compounds 4a-c. The different CPIls were prepared by substitution of the chloride groups in polymer 2 by several chiral imidazoles derived from amino acids (CILs 3a-c). As an example, a flask was charged with 0.1513 g (0.588 mmol) of CIL-3a and 0.0603 g (0.395 mmol) of 2. The mixture was dissolved in 3 mL of 2-Me-THF. The reaction was allowed to proceed at 40 °C for 4 days. The product precipitates during the reaction. After that, it was redissolved in MeOH and was isolated by precipitation with Et₂O to yield CPIl-4a (62 %).

Scheme S.I.2 Anion exchange
Preparation of compound 5. A flask was charged with 0.1746 g (0.426 mmol) of CPIL-4a and it was dissolved in 5 mL of MeOH. Then, 0.1478 g (0.515 mmol) of LiNTf₂ were added. The reaction was allowed to proceed at room temperature for 24 hours, after which the product CPIL-5 was purified by dialysis against MeOH and isolated by evaporation.

\[ \text{1H-NMR Spectra} \]

\[ \text{1H NMR (500 MHz, CD}_3\text{OD)} \delta 7.86 (s, 1H), 7.60 (s, 1H), 7.41 – 6.92 (m, 8H), 6.43 (s, 2H), 5.41 (s, 1H), 4.58 – 4.13 (m, 2H), 2.48 (s, 1H), 1.01 (s, 3H), 0.78 (s, 3H). \]
$^1$H NMR (300 MHz, CD$_3$OD) $\delta$ 7.99 – 7.50 (m, 2H), 7.40 – 6.85 (m, 2H), 6.78 – 6.21 (m, 2H), 5.46 (s, 2H), 4.62 – 4.41 (m, 1H), 3.16 – 2.95 (m, 2H), 2.49 (s, 1H), 1.48 (s, 2H), 1.32 (s, 2H), 1.08 (s, 3H), 0.87 (s, 6H).

$^1$H NMR (300 MHz, CD$_3$OD) $\delta$ 7.72 (s, 2H), 7.42 – 6.77 (m, 12H), 6.75 – 6.19 (m, 2H), 5.65 – 5.12 (m, 2H), 4.65 – 4.07 (m, 3H), 3.50 (s, 2H), 2.00 – 1.20 (m, 3H).
**H NMR** (500 MHz, CD$_3$OD) δ 7.77 (s, 1H), 7.44 (s, 1H), 7.35 – 6.89 (m, 7H), 6.82 – 6.24 (m, 2H), 5.39 (s, 2H), 4.75 (s, 1H), 4.46 (s, 1H), 4.30 (s, 1H), 2.49 (s, 1H), 1.04 (s, 3H), 0.86 (s, 3H).

**IR Spectra**

**IR (ATR):** 3385, 3217, 3056, 2969, 2931, 1675, 1551, 1452, 1360, 1226, 1154, 1120, 1024, 821, 749, 700 cm$^{-1}$
**IR (ATR):** 3274, 3216, 3051, 2960, 2930, 2872, 1675, 1557, 1512, 1456, 1421, 1394, 1372, 1153, 1092, 612 cm\(^{-1}\)

**IR (ATR):** 3360, 3203, 3029, 2927, 2853, 1681, 1555, 1512, 1496, 1453, 1424, 1360, 1295, 1267, 1228, 1153, 1027, 822, 741, 699, 639 cm\(^{-1}\)
IR (ATR): 3380, 3319, 3147, 3058, 3033, 2969, 1680, 1550, 1460, 1429, 1346, 1136, 1053, 821, 740, 698, 615 cm\(^{-1}\)
DSC Results

**Fig. S.1.1** DSC curves for the different polymers prepared: 3rd heating cycle

Measurements of glass-transition temperatures were carried out on a Perkin Elmer differential scanning calorimeter (DSC), model DSC8. The instrument was calibrated for temperature and heat flow with zinc and indium reference samples provided by Mettler–Toledo. Samples were placed in a 40 mL hermetically sealed aluminum pan with a pinhole at the top of the pan. An empty aluminum pan was used as the reference. The samples inside the differential scanning calorimeter furnace were exposed to a flowing N₂ atmosphere. Before the DSC test, each sample was dried at 90–100 ºC and 10⁻²⁻¹⁻³ mbar for 4 h, and was further dried in situ on the differential scanning calorimeter by holding the sample at 120 ºC for 15 min. This is important because the presence of volatiles, especially water, can affect the glass-transition and melting temperatures. Melting transition temperatures were determined by multiple cycles of heating from 40°C to 180°C, followed by cooling from 180°C to 40°C both at a rate of 10°C min⁻¹. The Tₘ temperatures were determined as the onset of the transition.
Fig. S.I.2 Turbidity curves of CPILs-4 at 0.5 mg/mL in CHCl₃. Variation of transmittance with temperature at 600 nm.
Fig. S.I.3 $^1$H-NMR (500 MHz, CDCl$_3$) spectra of CPIL-4a at 1.0 mg/mL + 0.5% EtOH.
(a) 30 °C, (b) 40 °C, (c) 55 °C, (d) 75 °C
Fig. S.I.4 TEM images of AuNPs. a) AuNPs- Poly(VBC) 2, b) AuNPs-CPIL-4a after modification of AuNPs- Poly(VBC) 2. Both of them have a 3 nm particle size and are unaggregated because of the stabilization by the polymer.
Fig. S.I.5 Computational models for CPIL-4a based on the organization through the formation of C2-H⋯Cl⋯⋯H-NCO interactions between vicinal groups in the side chain. A) CPK model showing the orientation of the vicinal aromatic rings on the main chain; the structure of the C2-H⋯Cl⋯⋯H-NCO pattern is illustrated in the case shown inside the yellow rectangle. B) CPK representation of the aromatic rings on the main chain.