Self-assembly and Complexation of Cellulose/Ionic Liquid at High Cellulose Concentration: Anion Dependence

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Experimental details

IL synthesis

The ILs, $[C_3mim][Cl]$, $[C_3mim][OAc]$, and $[C_3mim][DMP]$, were synthesized referring to previous reports.¹⁻³ 1-methylimidazole and 1-chloropropane were mixed and stirred in acetonitrile or ethyl acetate at 353 K for 6 days under an inert atmosphere. The solution was evaporated to remove the solvent, and the residue was washed with ethyl acetate more than 5 times. Then $[C_3mim][Cl]$ was obtained, which was recrystallized with acetonitrile once. For the $[C_3mim][OAc]$ preparation, an aqueous solution of acetic acid was passed through a column filled with anion-exchange resin (Amberlite® IRN78 hydroxide form) in distilled water until pH became constant. After unreacted acetic acid was washed off with distilled water, $[C_3mim][OAc]$ was passed through the column until no precipitation was observed with AgNO₃ aqueous solution. Liquid $[C_3mim][OAc]$ was obtained by evaporation. $[C_3mim][DMP]$ was prepared by stirring acetonitrile solution of 1-propylimidazole and trimethylphosphate at 353 K for 6 days. The solution was evaporated and the remained liquid was washed with ethyl ester 5 times. All the ILs were characterized by ¹H and ¹³C NMR (vide infra), and vacuum dried with heating before use. The water content of $[C_3mim][Cl]$, $[C_3mim][OAc]$, and $[C_3mim][DMP]$ was estimated to be 0.33 wt%, 0.22 wt%, and 0.14 wt%, respectively, by the Karl Fischer titration (MKC-501, Kyoto Electronics).

Cellulose/IL mixing

A certain amount of IL was added in 0.2 g of dried cellulose (Avicel) in a glass vial. The dried cellulose was obtained by vacuum-drying with heating, and the water content was estimated to be less than 1 wt% by thermogravimetric-differential thermal analysis (TG/DTA). They were mechanically mixed by a spatula until the mixture became visually homogenous (c.a., 5 min) at 297 \pm 2 K. The mixture containing [C₃mim][OAc] or [C₃mim][DMP] was then heated at 353 \pm 5 K for 1 h. Since [C₃mim][Cl] was sometimes crystallized at room temperature, the heating temperature of 393 K was employed to achieve complete melting of the IL. The mixture was placed in a Teflon cell with a 0.5-mm thickness for X-ray scattering measurements. The cell was sandwiched between two sheets of Kapton film (5 µm thickness) and sealed with glue. These processes were all performed in an Ar atmosphere glovebox.

X-ray and thermal analysis

X-ray scattering measurements were performed with NANO-Viewer (Rigaku). A Cu K α radiation source ($\lambda = 0.154$ nm) was used at an applied voltage of 40 kV and a filament current of 30 mA. All the patterns were recorded with 1 hour irradiation at 295 ± 2 K. For differential scanning calorimetry measurements (DSC7020, Hitachi High-Tech Science), the sample was packed in an aluminum cell and mechanically sealed. The DSC traces were obtained at a scanning rate of 5 K/min. TG/DTA measurements were performed with STA7200 (Hitachi High-Tech Science) at a scanning rate of 10 K/min under N₂ atmosphere.

NMR characterization

[C₃mim][Cl]

¹H-NMR (Chloroform-*d*): δ (in ppm) = 10.0 (1H, s, NCHN), 7.41 (1H, s, NCHCH), 7.32 (1H, s, NCHCH), 3.93 (2H, t, NCH2CH2CH3), 3.74 (3H, s, NCH3), 1.59 (2H, m, NCH2CH2CH3), 0.58 (3H, t, NCH2CH2CH3). ¹³C-NMR (Chloroform-*d*): δ (in ppm) = 137.8 (s, NCHN), 123.7 (s, NCHCH), 122.1 (s, NCHCH), 51.4 (s, NCH2CH2CH3), 36.6 (s, NCH3), 23.7 (s, NCH2CH2CH3), 10.8 (s, NCH2CH2CH3).

[C₃mim][OAc]

¹H-NMR (DMSO-*d*₆): δ (in ppm) = 10.33 (1H, s, NCHN), 7.95 (1H, s, NCHCH), 7.87 (1H, s, NCHCH), 4.13 (2H, t, NCH2CH2CH3), 3.86 (3H, s, NCH3), 1.73 (2H, m, NCH2CH2CH3), 1.54 (3H, s, CH3COO), 0.76 (3H, t, NCH2CH2CH3).

¹³C-NMR (DMSO- d_6): δ (in ppm) = 173.7 (s, COCH3), 138.7 (s, NCHN), 124.1 (s, NCHCH), 122.8 (s, NCHCH), 50.4 (s, NCH2CH2CH3), 35.9 (s, NCH3), 26.8 (s, COCH3), 23.4 (s, NCH2CH2CH3), 10.9 (s, NCH2CH2CH3).

[C₃mim][DMP]

¹H-NMR (Chloroform-*d*): δ (in ppm) = 10.1 (1H, s, NCHN), 7.45 (1H, s, NCHCH), 7.32 (1H, s, NCHCH), 4.00 (2H, t, NCH2CH2CH3), 3.81 (3H, s, NCH3), 3.34 (6H, s, POCH3) 1.67 (2H, m, NCH2CH2CH3), 0.71 (3H, t, NCH2CH2CH3).

¹³C-NMR (Chloroform-*d*): δ (in ppm) = 138.4 (s, NCHN), 123.6 (s, NCHCH), 122.0 (s, NCHCH), 52.0 (2C, s, POCH3), 50.7 (s, NCH2CH2CH3), 35.8 (s, NCH3), 23.3 (s, NCH2CH2CH3), 10.4 (s, NCH2CH2CH3).

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mol%	10.0	15.0	20.0	25.0	30.0	40.0	50.0	60.0	80.0
wt%	11.2	16.7	22.1	27.5	32.7	43.1	53.2	63.0	82.0



Figure S1. Sample appearance of cellulose/ $[C_3mim][OAc]$ (top), cellulose/ $[C_3mim][DMP]$ (middle), and cellulose/ $[C_3mim][Cl]$ (bottom) mixtures. The cellulose concentrations are 10 mol%, 15 mol%, 20 mol%, 25 mol%, 30 mol%, 40 mol%, 50 mol%, 60 mol%, and 80 mol% from left to right, as labeled on each screw vial.



Figure S2. Differential scanning calorimetry traces of pure $[C_3mim][DMP]$. Only a glass transition was observed at ca. 212 K.



Figure S3. Water content estimation with TG/DTA for (a) cellulose/ $[C_3mim][DMP]$, (b) (c) cellulose/ $[C_3mim]Cl$, corresponding to Figure 4.



Figure S4. Water content estimation with TG/DTA for undried cellulose.



Figure S5. Optimized model structure of the cellulose-anion sheet, (a) cellulose/[C₃mim][OAc], (b) cellulose/[C₃mim][DMP], and (c) cellulose/[C₃mim]Cl, calculated by the ONIOM method (B3LYP/6-311++G(d,p):PM6). The upper (B3LYP) and lower (PM6) layers represent the ball frame and the wire frame, respectively. For the calculations, the Gaussian09 program packeage was used.⁴ The periodic distance was estimated based on the cellobiose rings (ten carbon and three oxygen atoms). All the structures produced no imaginary frequency. It is noted that the optimized structure of the cellulose/[C₃mim][OAc] model is slightly different from the one previously reported.⁵

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