Efficient and Rapid Direct Transesterification Reactions of Cellulose with Isopropenyl Acetate in Ionic Liquids

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SUPPORTING INFORMATION

Experimental Section

Materials. The 1-ethyl-3-methyl-imidazolium acetate (EmimOAc) was available from Kanto Chemical Co., Inc., and used without further purification. The isopropenyl acetate was available from the Sigma-Aldrich Chemicals Co., and used as received. As a cellulose source, Avicel PH-101 was purchased from Sigma-Aldrich Chemicals Co. The apparent molecular weight of the avicel was determined by SEC measurements in THF with PSt calibrations of carbanilated cellulose sample (reacted with phenyl isocyanate). The carbanilation reaction was carried out according to a previously reported method.[1] The apparent number average degree of polymerization of original cellulose was calculated to be 105. All other chemicals were commercially available and used without further purification unless otherwise stated.

Instruments. All the ^{1}H and ^{13}C NMR spectra in solution were recorded by JEOL 400 and 600 MHz FT-NMR spectrometers in deuterated solvents, and the chemical shifts (δ) were given in ppm as either the solvent peak or TMS as the internal standard. The size exclusion chromatography (SEC) was performed at 40 ˚C in $CHCl_3$ at the flow rate of 1.0 $mL \cdot min^{-1}$. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. The IR spectra were recorded by a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR unit.

Experimental Procedures.

Transesterification reaction of cellulose in EmimOAc. A typical reaction based on the transesterification of cellulose was carried out as follows: A 1-ethyl-3-methyl-imidazolium acetate (EmimOAc) solution (20 g) of cellulose (600 mg, $[\text{monomeric unit}]_0 = 3.7$ mmol) was dried overnight under vacuum conditions at 80 ˚C. After the drying process was finished, isopropenyl acetate (20 mL) was added under an Ar atmosphere. After the reaction mixture was stirred overnight, the reaction mixture was diluted with CH_2Cl_2 and poured into a large amount of MeOH. The polymer was purified by reprecipitation (CH_2Cl_2/MeOH) to yield a pale yellowish powder. Yield: 843 mg (79.0 %).

Control Experiment; transesterification reaction of cellulose in 1-butyl-3-methylimidazolium chloride (BmimCl). A BmimCl solution (4 g) of cellulose (120 mg, $[\text{monomeric unit}]_0 = 0.74$ mmol) was dried overnight under vacuum conditions at 80 ˚C. After the drying process was finished, isopropenyl acetate (4 mL) was added under an Ar atmosphere. After the reaction mixture was stirred overnight, the reaction mixture was poured into a large amount of MeOH. The FT-IR spectrum of the recovered product was depicted in ***Figure S-2***.

Control Experiment; transesterification reaction of cellulose in EmimOAc in the presence of water. An EmimOAc solution (4 g) of cellulose (120 mg, $[\text{monomeric unit}]_0 = 0.74$ mmol) was dried under vacuum conditions at 80 ˚C. After the drying process was finished, 2 mL of water and subsequently isopropenyl acetate (2 mL) were added under an Ar atmosphere. After the reaction mixture was stirred for 1 hour, the reaction mixture was poured into a large amount of MeOH. The FT-IR spectrum of the recovered product was depicted in ***Figure S-3***.

Determination of degree of substitution (DS) values of cellulose acetates. The degree of the substitution (DS) values of the cellulose acetate was determined by ^{1}H NMR measurements of the cellulose derivatives that were obtained by the reaction of cellulose acetate with an excess amount of benzoyl chloride. The typical procedure is as follows: A 4 mL $CHCl_3$ solution of the cellulose acetate (100 mg, 347 μmol), benzoyl chloride (440 mg, 3.1 mmol) and triethylamine (318 mg, 3.1 mmol) was stirred for 25 hours at r.t.. The reaction mixture was then poured into a large amount of MeOH. The obtained precipitate was collected and dried under vacuum conditions. Isolated yield: 75.2 mg (75.2 %).

The DS values were calculated using the following equation:

$$DS = 3 \times \frac{peak\ area_{1.5\sim2.3ppm}/3}{peak\ area_{1.5\sim2.3ppm}/3 + peak\ area_{7\sim8.5ppm}/5}$$

In order to avoid potential overlapping of the aromatic protons and solvent peak, NMR measurements were conducted in DMSO-d_6. Figure *S-1* in the supporting information shows a representative ^{1}H NMR spectrum of the cellulose derivative that was obtained by the reaction of cellulose triacetate with an excess amount of benzoyl chloride.

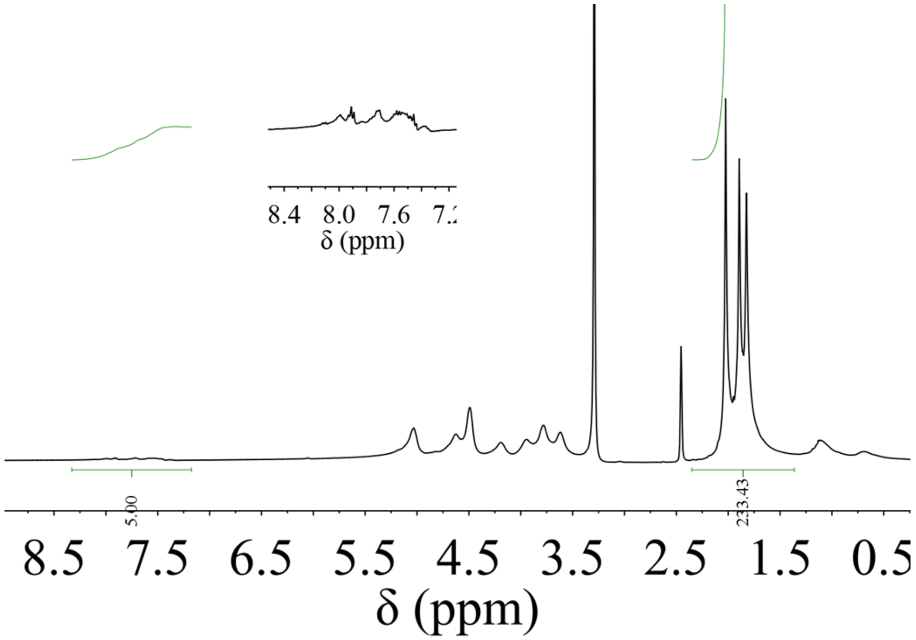

Figure S-1. ^{1}H NMR spectrum of the cellulose derivative that was obtained by the reaction of cellulose triacetate with an excess amount of benzoyl chloride measured in DMSO-d_6.

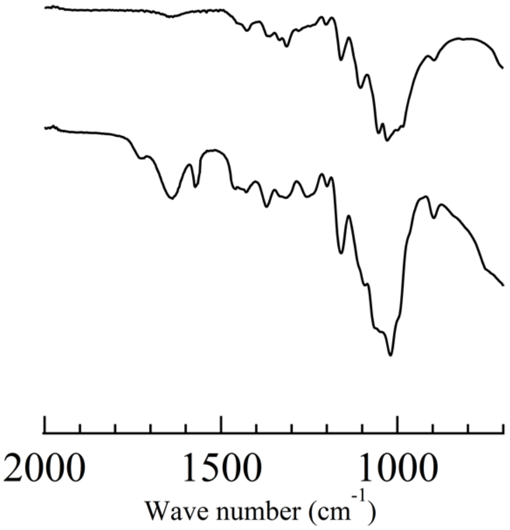

Figure S-2. ATR-mode FT-IR spectra of original cellulose (upper) and the recovered polymer after the reaction with IPA in BmimCl (lower).

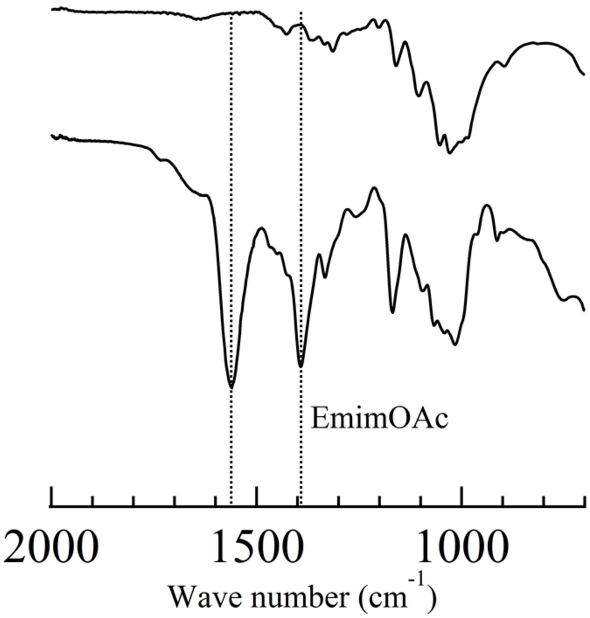

Figure S-3. ATR-mode FT-IR spectra of original cellulose (upper) and the recovered polymer after the reaction with IPA in EmimOAc in the presence of water (lower).

Reference

1. Schlufter, K.; Schmauder, H.-P.; Dorn, S.; Heinze, T., *Maromol. Rapid Commun.* **2006,** *27* (19), 1670-1676.