Supporting Information

Poly(oxyalkylene) synthesis in Brønsted Acid Ionic Liquids

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Experimental Part

Chemicals

1-butylimidazolium (Aldrich, 98%), 1-octylimidazolium (Iolitec, >99%), 1,4-butanesultone (Aldrich, >99%), bis-(trifluoromethylsulfonyl)imide (Iolitec, 99%, in 80% aqueous solution), 1,12-dodecanediol (99%, Sigma-Aldrich), 1,10-decanediol (98%, Sigma-Aldrich), 1,9-nanonediol (99%, Sigma-Aldrich), 1,8-octanediol (98%, ABCR), 1,7-heptanediol (98%, ABCR), 1,6-hexanediol (99% Sigma-Aldrich), 1,4-butanediol (99%, Alfa Aesar) were also used without any further purification.

Synthesis of BAILs

Brønsted acid ionic liquids (BAILs) used in the investigation were synthesized according to a two-step approach:[1, 2]

The zwitterions were synthesized by mixing 1-alkylimidazolium with 1 mole equivalent of 1,4-butanesultone, with reflux in ethyl acetate. 4-(3'-butyl-1'-imidazolio)-1-butanesulfonate, precipitated in the reaction medium. It was then washed with ethyl acetate and diethyl ether, while 4-(3'-octyl-1'-imidazolio)-1-butanesulfonate, was recrystallized in acetone/hexanol (0.86/0.14 vol/vol) mixture. The zwitterions were obtained in 95-98% yields as white solids.

The second step is demonstrated as follows: in a round flask, 4-(3'-alkyl-1'-imidazolio)-1-butanesulfonate was mixed with 1 mol equivalent of bis-(trifluoro methylsulfonyl)imide $(CF_3SO_2)_2NH$). The flask was first heated in a water bath at 80 °C; once the mixture melted, residual water in reaction medium was eliminated under vacuum (60 mbar). The two 4-(3'-alkyl-1'-imidazolio)-1-butanesulfonic acid bis(trifluoro-methylsulfonyl)imidides were obtained in quantitative yields.

Polyetherification of diols (m>6)

The polyetherification of 1,12-dodecanediol in 4-(3'-butyl-1'-imidazolio)-1-butanesulfonic acid bis-(trifluoromehylsulfonyl)imidide ([BBSIm]Tf_2N) is given as an example: 1 mmol of [BBSIm]Tf_2N (0.5415 g) was blended with 2 mmol of 1,12-dodecane diol (0.4047 g) in a glass tube with a magnetic headcross stirrer. The mixture was maintained at 130°C under nitrogen flow (200 ml/min) for a predetermined time (50 to 96 h). The reaction medium was then cooled down to room temperature and methanol (10 mL) added to solubilize the BAIL with the help of an ultrasonic bath. The insoluble polyether was filtrated, washed with 2x10 ml of methanol and dried at 40 °C under vacuum overnight. As around 20% of 1,12-dodecanediol was evaporated with the N_2 flow, the recovered yield of each reaction was less than 80%. The loss of 1,12-dodecanediol was calculated from the mass difference of the reaction medium before and after the reaction, and the percentage of lost mass was calculated accordingly.

Reaction of 1,6-hexane diol and 1,4-butane diol

The reaction of these two diols in 4-(3'-butyl-1'-imidazolio)-1-butanesulfonic acid bis-(trifluoromehylsulfonyl)imidide ([BBSIm]Tf_2N) is demonstrated with that of 1,6-hexanediol as an example: 1 mmol of [BBSIm]Tf_2N (0.5415 g) was blended with 2 mmol of 1,6-hexane diol (0.2364 g) in a glass tube with a magnetic headcross stirrer. The mixture was maintained at 130°C under nitrogen flow (200 ml/min) for a predetermined time (50 to 60 h). The volatile composition was distilled and collected in a trap equiped with liquid nitrogen. The reaction medium was then cooled down to room temperature and methanol (10 mL) added to solubilize the BAIL with the help of an ultrasonic bath. The insoluble polyether was filtrated, washed with 2x10 ml of methanol and dried at 40 °C under vacuum overnight.

Analytical Methods

NMR Spectroscopy: The ^1H NMR spectra and 2D ^1H-^1H COSY-45 NMR spectra of monomers and polymers were recorded on Bruker Avance 500 spectrometer in chloroform-*d* (ref. δ ($CHCl_3$) = 7.26 ppm), while the spectra of 4-(3'-alkyl-1'-

imidazolio)-1-butanesulfonic acid bis-(trifluoromethylsulfonyl)imidide ([RBSIm]Tf_2N) were recorded in D_2O/TSP-d_4 (ref. δ(TSP-d_4) = 0 ppm). ^{19}F NMR spectra were recorded on a Bruker Avance 300 spectrometer in chloroform-*d* (ref. δ(C_6F_6)= -164.9 ppm).

Size Exclusion Chromatography (SEC): SEC was used to determine the number-average and mass-average molar masses of polymers, Mn and Mw, respectively. The SEC equipment consisted of a Waters 515 HPLC pump, a Waters 410 RI detector and a set of five Ultrastyragel columns ($50+500+10^3+10^4+10^5$Å). CH_2Cl_2 was used as eluting solvent with a flow rate of 1 mL/min at room temperature. Each sample was prepared with 8 mg of polymer, 1 mL of CH_2Cl_2 and 1 μL of toluene. 100 μl of sample solution was injected for each analysis. The system was calibrated with polystyrene standards.

Differential Scanning Calorimetry (DSC) was performed on a TA Instruments 9900 apparatus equipped with a DSC910 module using the following heating/cooling cycles: (1) heating from -85°C to 210°C at 20°C/min, (2) cooling to -85°C at 20°C/min. (3) heating from –85°C to 210°C at 10°C/min. Experiments were run under nitrogen atmosphere at low temperature by means of a liquid nitrogen cooling accessory LNCA-II. Melting temperatures (T_m) were taken at the minima of the melting endotherms of the second run.

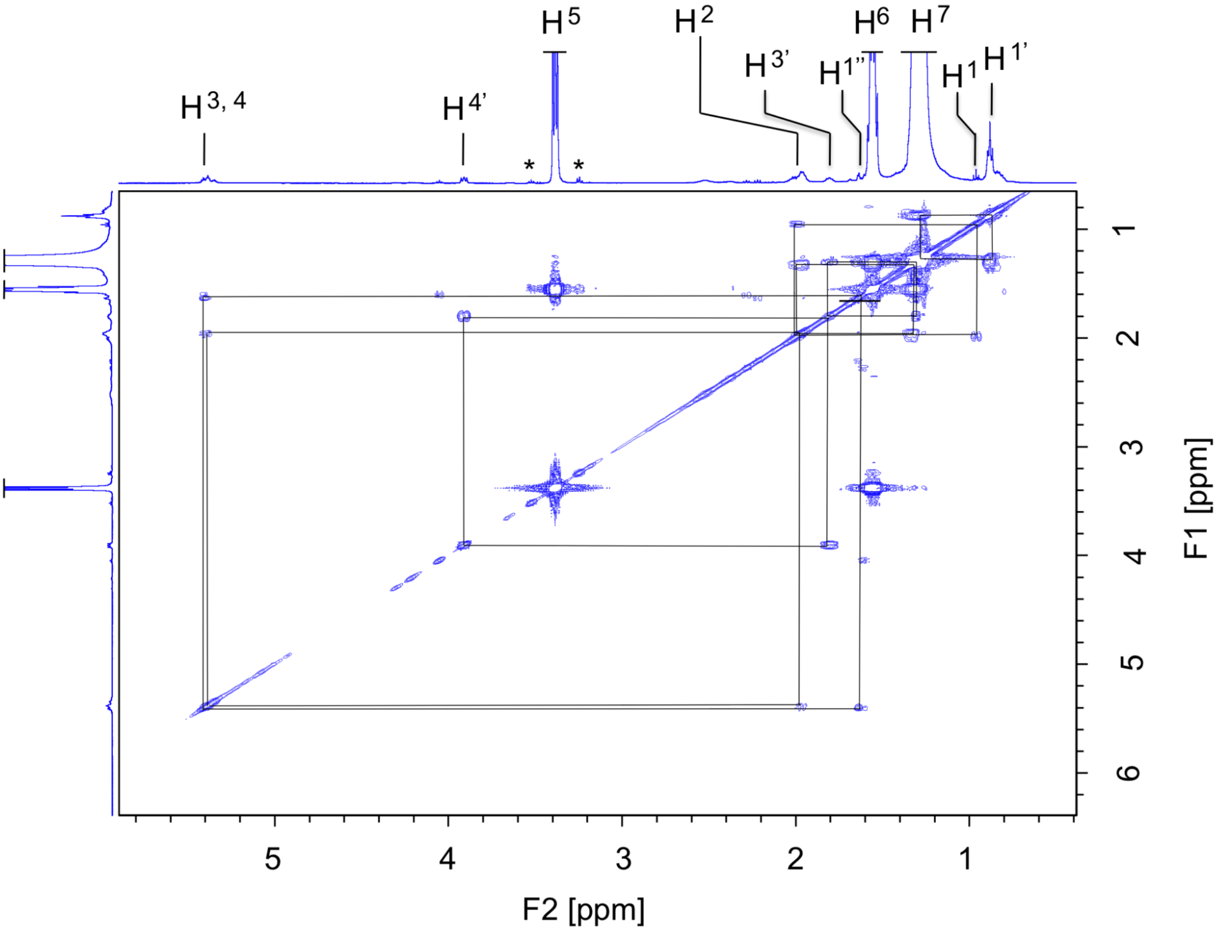

Fig.1. 2D ^{1}H-^{1}H COSY-45 NMR spectrum (500 MHz, $CDCl_3$) of purified poly(oxydodecamethylene). Reaction carried out at 130 °C, diol/BAIL= 2/1, 63 h in [OBSIm]Tf_2N under N_2 flow (200 ml/min), * : ^{13}C satellites

Unsaturations in α : Correlation $H^{1''}$-$H^{3,4}$
Unsaturations in β : Correlations H^{2}-$H^{3,4}$ and H^{1}-H^{2}
Unsaturations in γ : Correlations $H^{1'}$-H^{7}, H^{2}-H^{7} and H^{2}-$H^{3,4}$

Hydroamination in γ or δ: Correlations $H^{4'}$-$H^{3'}$ and $H^{3'}$-H^{7}
Hydroamination in β is not detected since no correlation is observed between protons close to $H^{3'}$ and protons close to H^{1}.

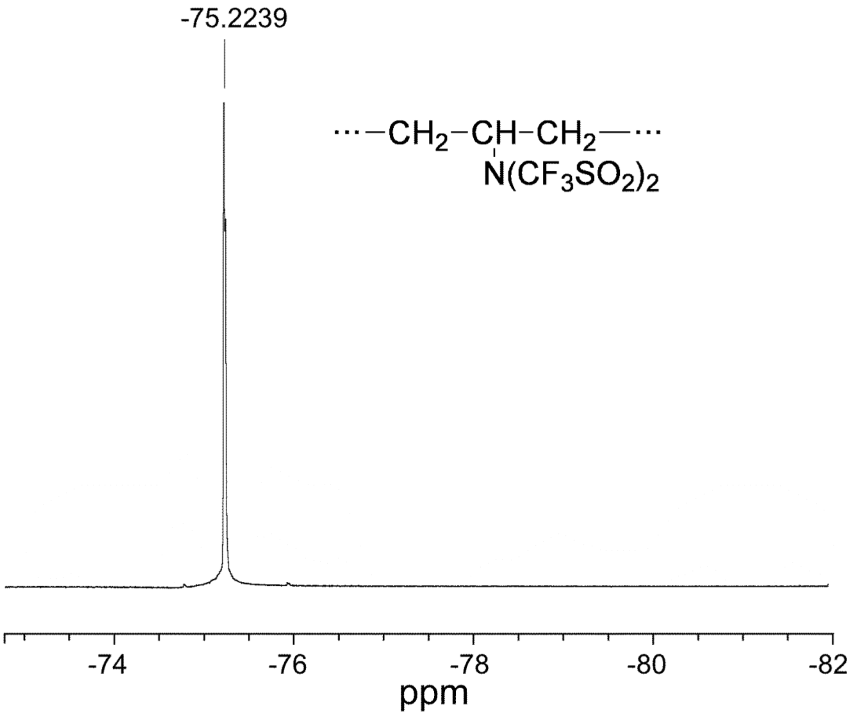

Fig. 2. ^{19}F NMR spectrum (300 MHz, $CDCl_3$) of purified poly(oxydodecamethylene), reaction undertaken at 130 °C, diol/BAIL= 2/1, 63 h in [OBSIm]Tf_2N under N_2 flow (200 ml/min)

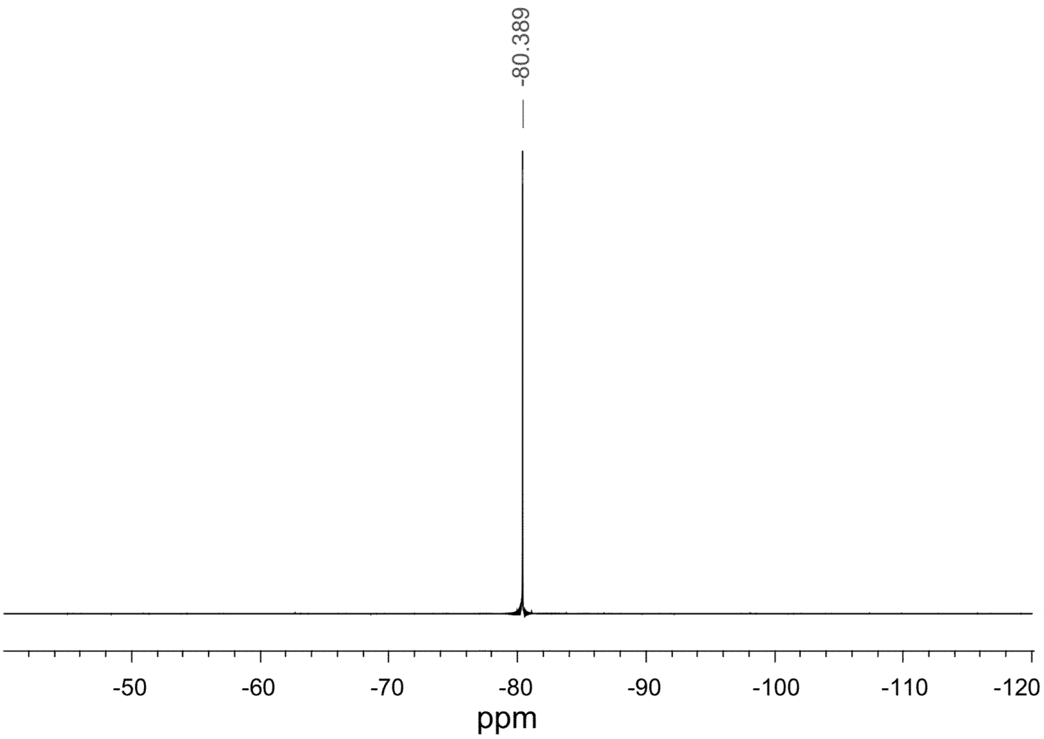

Fig. 3. ^{19}F NMR spectrum (300 MHz, $CDCl_3$) of [OBSIm]Tf_2N

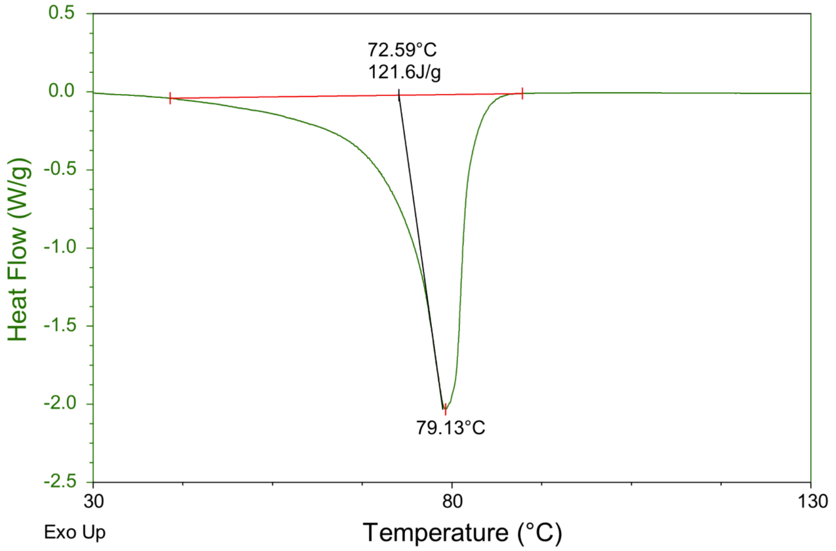

Fig. 4. DSC thermogram of purified poly(oxydodecamethylene), reaction undertaken at 130 °C, diol/BAIL= 2/1, 63 h in [OBSIm]Tf_2N under N_2 flow (200 ml/min)

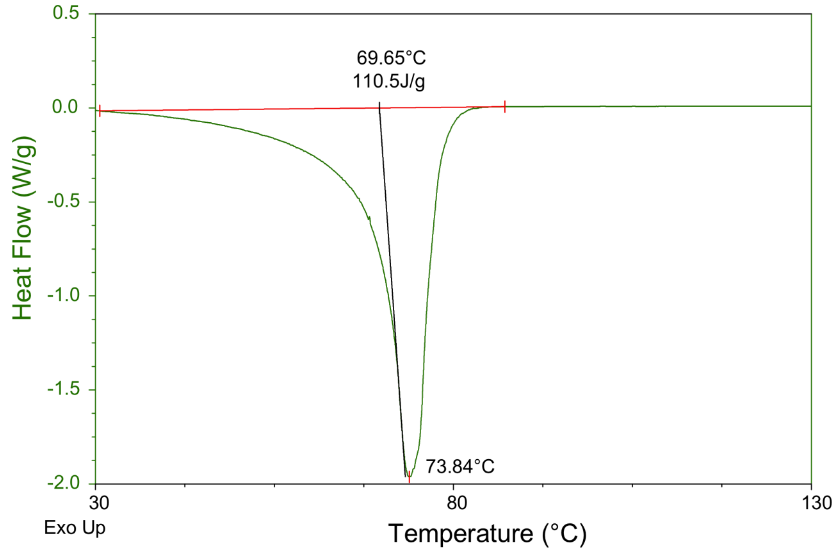

Fig. 5. DSC thermogram of purified poly(oxydecamethylene), reaction undertaken at 130 °C, diol/BAIL= 2/1, 50 h in [OBSIm]Tf_2N under N_2 flow (200 ml/min)

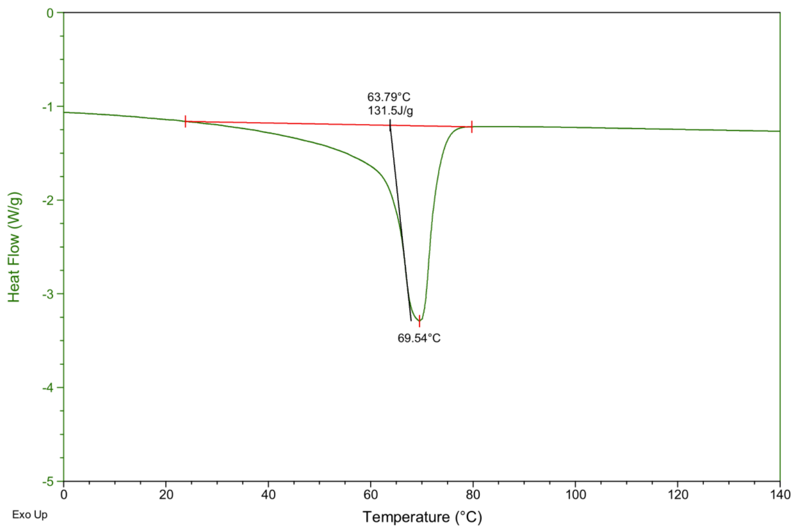

Fig. 6. DSC thermogram of purified poly(oxynonamethylene), reaction undertaken at 130 °C, diol/BAIL= 2/1, 50 h in [OBSIm]Tf_2N under N_2 flow (200 ml/min)

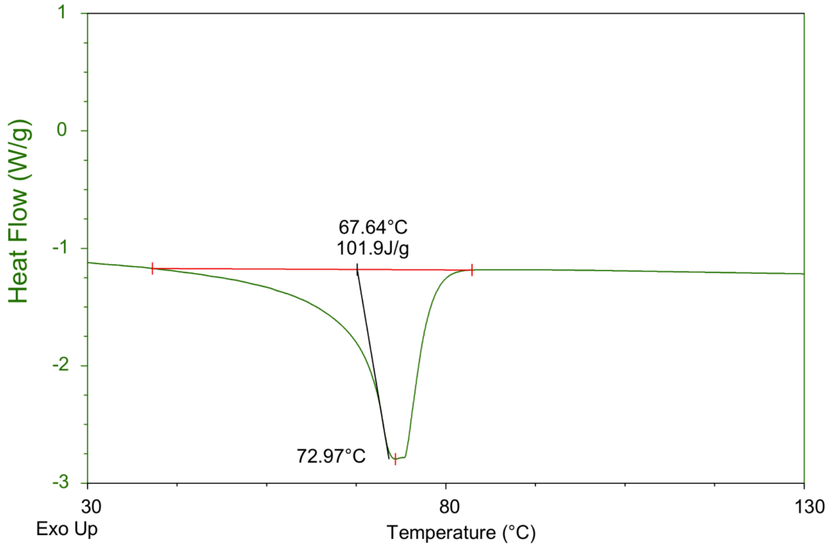

Fig. 7. DSC thermogram of purified poly(oxyoctamethylene), reaction undertaken at 130 °C, diol/BAIL= 2/1, 50 h in [OBSIm]Tf_2N under N_2 flow (200 ml/min)

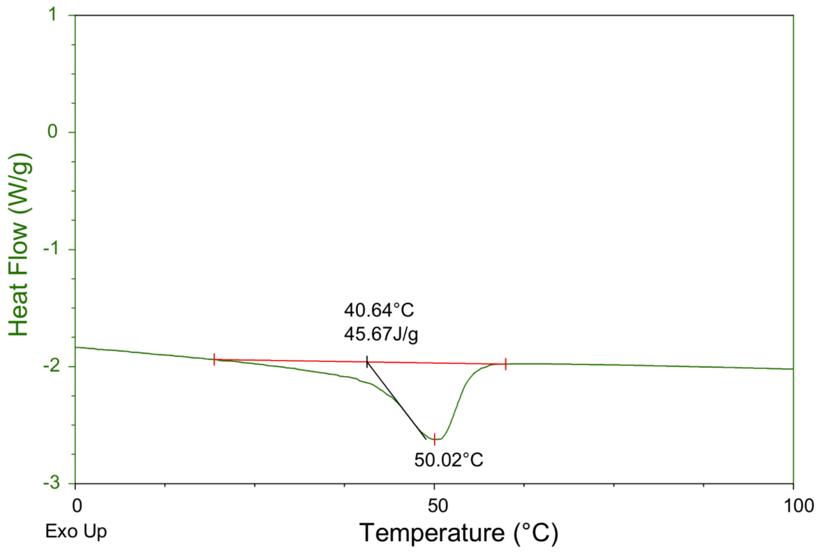

Fig. 8. DSC thermogram of purified poly(oxyheptamethylene), reaction undertaken at 130 °C, diol/BAIL= 2/1, 60 h in [OBSIm]Tf_2N under N_2 flow (200 ml/min)

References:

1. J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu and Z. Sun, *Catal. Commun.*, 2004, **5**, 473-477.
2. A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis-Jr., *J. Am. Chem. Soc.*, 2002, **124**, 5962-5963.