Designing melt flow of polyisobutylene ionic liquids

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Supporting information

1. Synthesis and characterization

S1 Synthetic procedure:

Synthesis of bromo telechelic PIB: A three-necked round-bottom flask equipped with mechanical stirrer, septum and stopcock was heated under vacuo several times and flushed intermittently with argon. Dry DCM (90 mL) and dry n-hexane (130 mL) were added to the flask via syringe. DtBP (0.24 mL, 1.07 mmol), DMA (0.099 mL, 1.07 mmol), TMPCl (0.768 mL, 4.5 mmol) and isobutylene (17.52 mL, 214 mmol) were added sequentially into the prechilled flask kept at -80 °C. The polymerization started upon addition of $TiCl_4$ (2 mL, 18 mmol) under argon atmosphere and was quenched after 20 minutes with the 1-bromo-3-phenoxy propane (2.18 mL, 13.5 mmol). After stirring for further 2 h at -80 °C, 20 mL methanol were added to the reaction mixture. The solvents were removed under vacuum and precipitation, three times in methanol, gave bromo-functionalized PIB **(1)** Yield: 94 % (11.28 g,).^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.27 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 4.08 (t, J = 5.8 Hz, 2H), 3.60 (t, J = 6.5 Hz, 2H), 2.31 (m, 2H), 0.99 (s, 15H) ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 156.3, 142.8, 127.1, 113.7, 65.3, 59.5, 58.2.

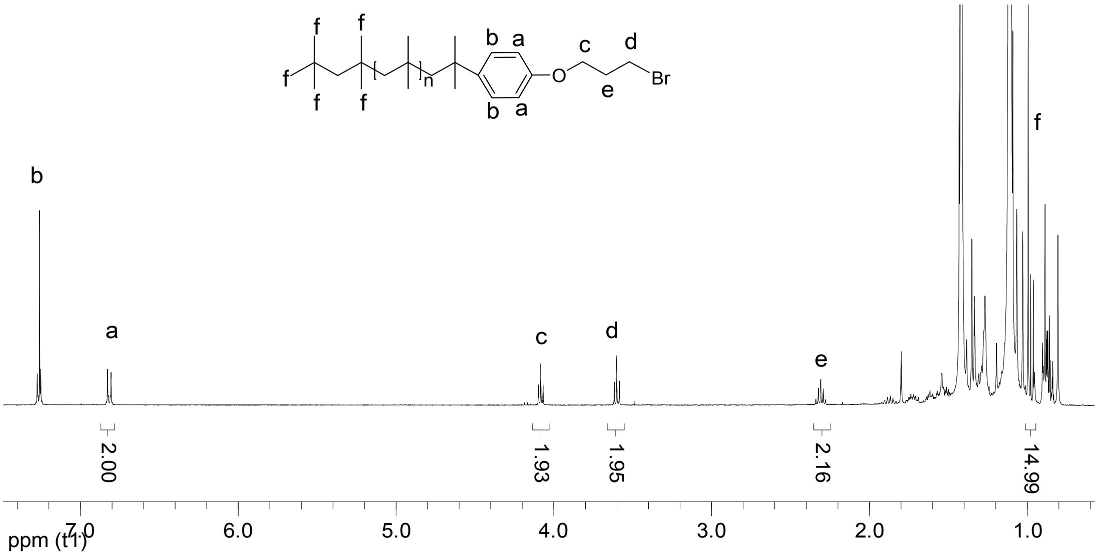
*Synthesis of azido- telechelic PIB (**1**):* The synthesis was accomplished according to Storey *et al.*[1] 2.5 eqv. of NaN_3 (0.351 g, 5.4 mmol) was added to a solution of bromine-functionalized PIB (5.4 g, 2.16 mmol) in heptane/DMF (20 mL / 20 mL) and stirred for 5 hours at 90 °C. After cooling and phase separation of the crude product, the heptane layer was washed with distilled water and finally precipitated in methanol to obtain a yield of 96 % (5.18 g) of polymer. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.27 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 4.08 (t, J = 5.8 Hz, 2H), 3.54 (t, J = 6.5 Hz, 2H), 2.07 (m, 2H), 0.99 (s, 15H).

*Synthesis of the 1-propargyl-3-methylimidazolium bromide (**3a**)*[2] 1-Methylimidazole (1.02 g, 12.43 mmol) was added drop wise to a solution of propargyl bromide (1.23 g, 10.36 mmol) in dry toluene (25 mL). After stirring the reaction mixture for 16 hours at 50 °C under nitrogen atmosphere, the resultant crude product was then purified by washing with toluene and ethyl acetate. Yield of 85.4 % (1.6 g), as a brownish powdered product was obtained.^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 10.38 (s, 1H), 7.57 (t, J = 1.7 Hz, 1H), 7.45 (t, J = 1.6 Hz, 1H), 5.36 (d, J= 2.5 Hz, 2H), 4.06 (s, 3H), 2.71 (t, J = 2.6 Hz, 1H).

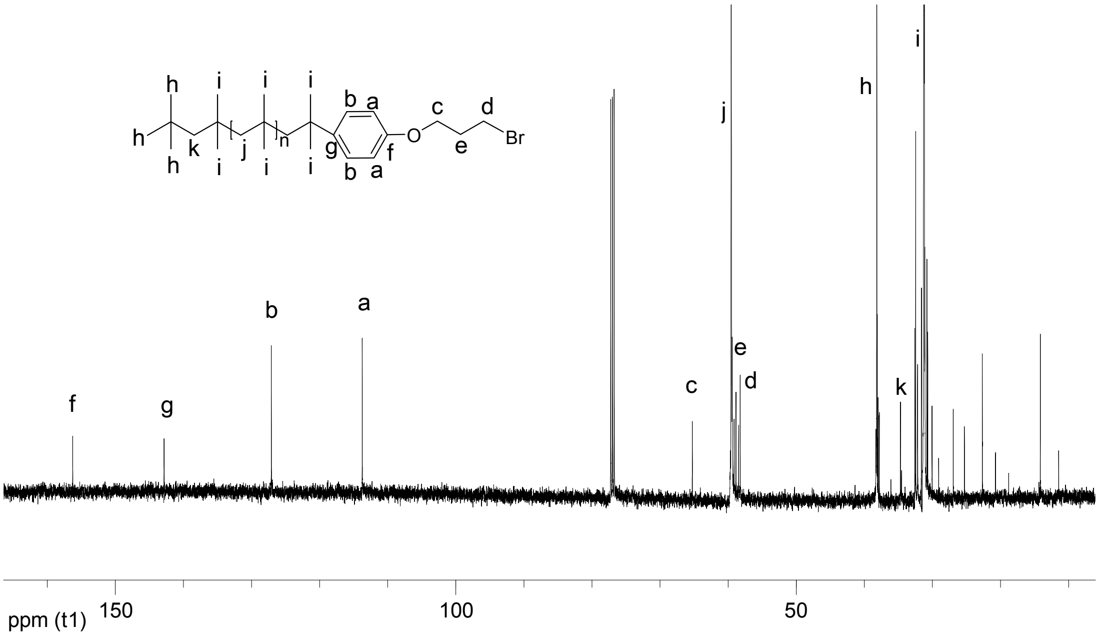
*Synthesis of the 1-propargyl-1-methylpyrrolidinium bromide (**3b**)*[2] 1.2 Eqv. of 1-Methylpyrrolidine (1.06 g, 12.43 mmol) was added to a solution of propargyl bromide (1.23 g, 10.36 mmol) in dry toluene (25 mL). The reaction mixture was stirred under inert atmosphere for 24 hours at 50 °C. Product purification by washing in toluene and ethyl acetate resulted into a slightly yellowish solid product. Yield: 85.2 % (1.7 g,).^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 4.87 (d, J = 2.5 Hz, 2H), 4.01 (dd, J = 6.9 Hz, J = 11.1 Hz, 2H), 3.85 (m, 2H), 3.45 (s, 3H), 2.85 (t, J = 2.5 Hz, 1H), 2.27 (m, 4H).

Synthesis of the N-propargyl-N,N,N-triethylammonium bromide ***(3c)***^{2} To a solution of propargyl bromide (1.23 g, 10.36 mmol) in dry toluene (20 mL) was added 1.2 eqv. of *N,N,N*-triethylamine (1.25 g, 12.72 mmol) and stirred at 50 °C under nitrogen atmosphere for 24 hours. Removal of solvent under vacuo and final purification by washing of crude product with toluene and ethyl acetate yielded a white solid product with a yield of 78.3 % (1.55 g).^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 4.60 (d, J = 2.5 Hz, 2H), 3.59 (q, $J_1=J_2=J_3$ = 7.3 Hz, 6H), 2.75 (t, $J_1=J_2$ = 2.5 Hz, 1H), 1.41 (t, $J_1=J_2$ = 7.3 Hz, 9H).

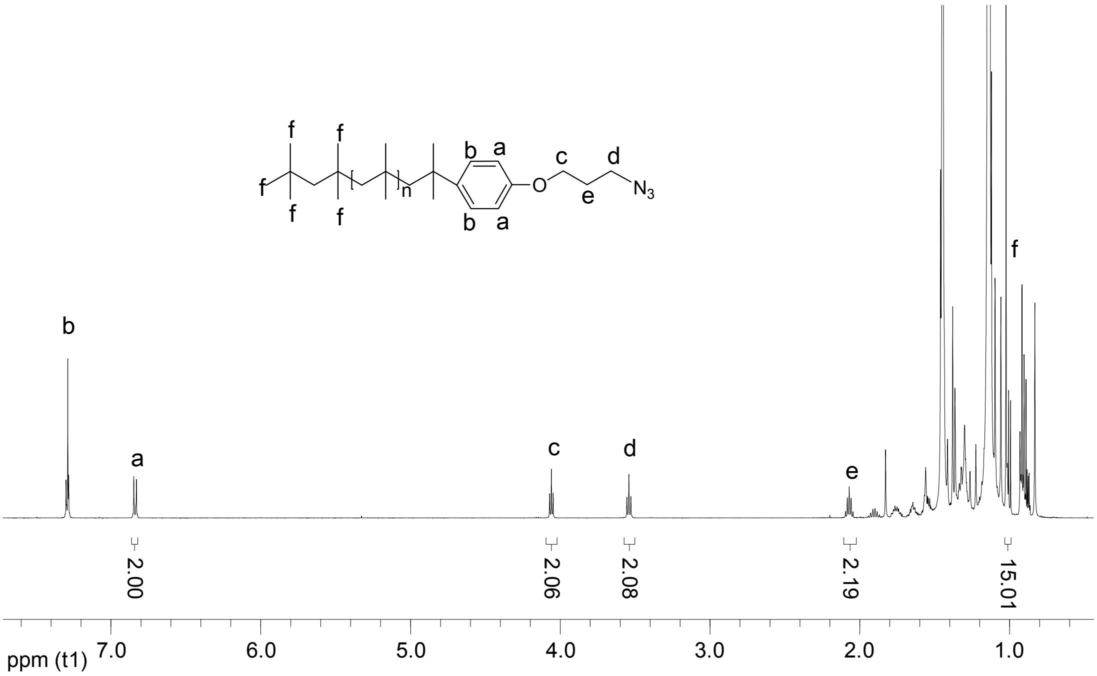
S2 ^{1}H- NMR spectrum of the bromo telechelic PIB (3000 g/mol).



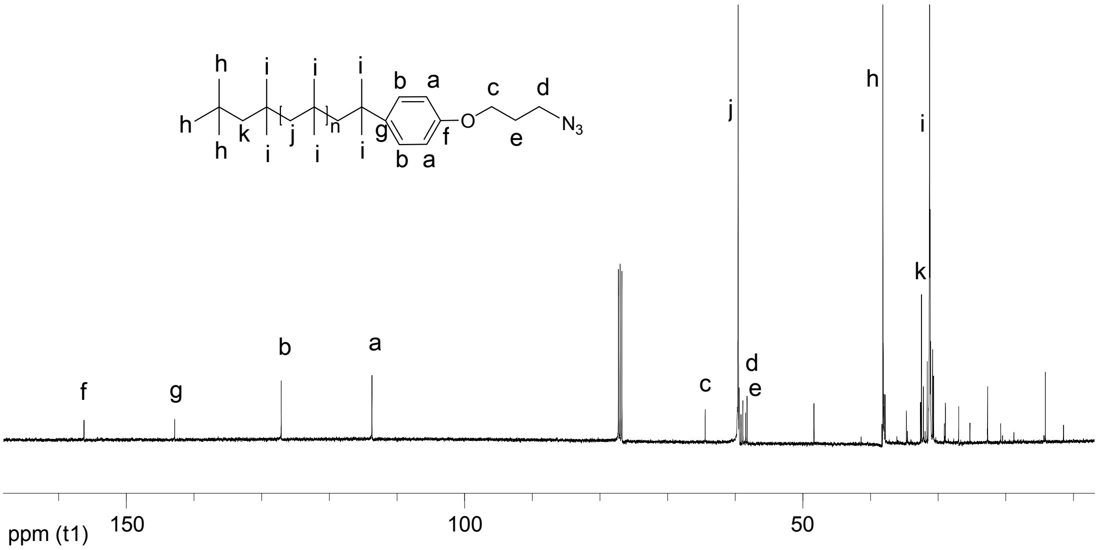
S3 ^{13}C- NMR spectrum of the bromo telechelic PIB (3000 g/mol).



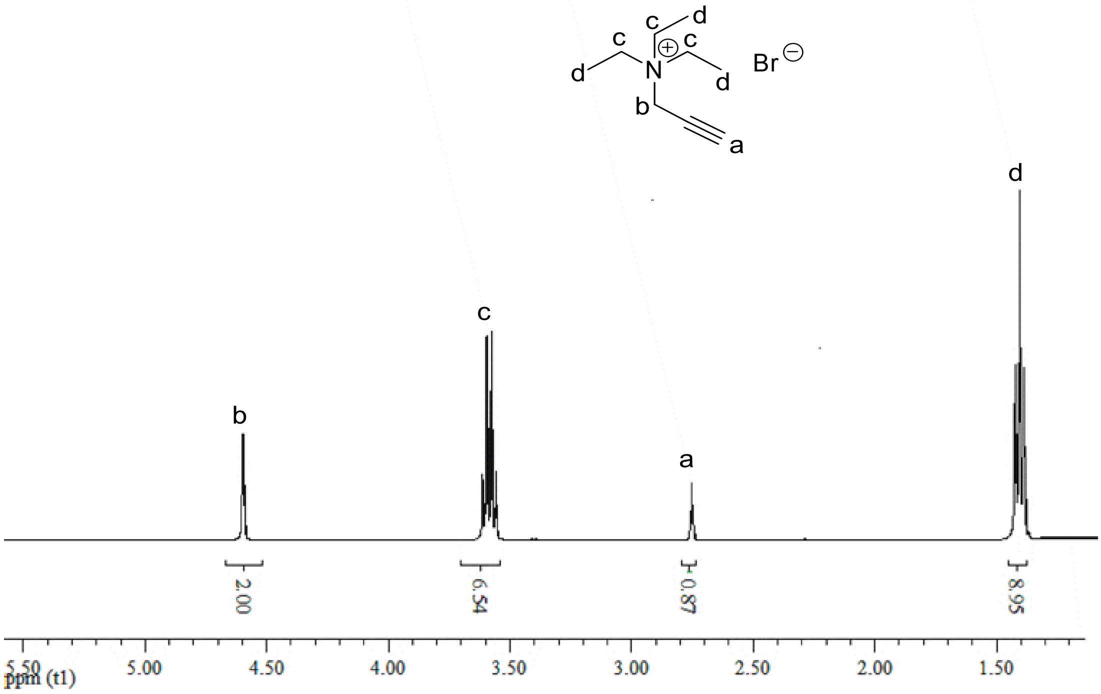
S4 ^{1}H- NMR spectrum of the azido telechelic PIB (**1**).



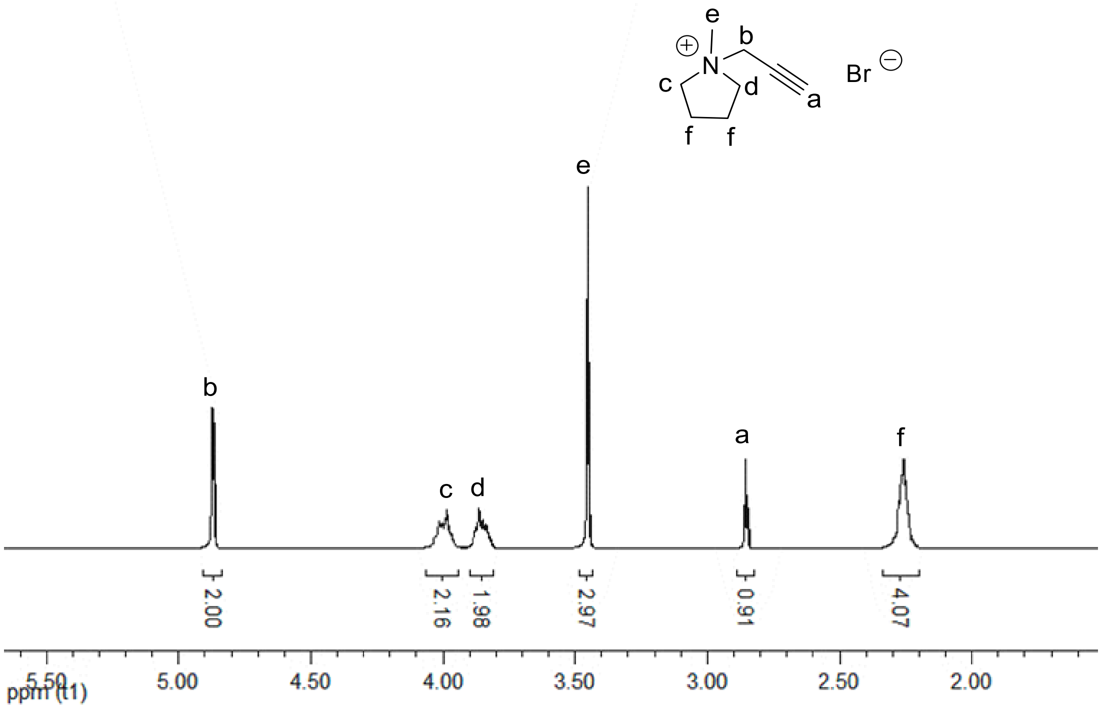
S5 ^{13}C- NMR spectrum of the azido telechelic PIB (**1**).



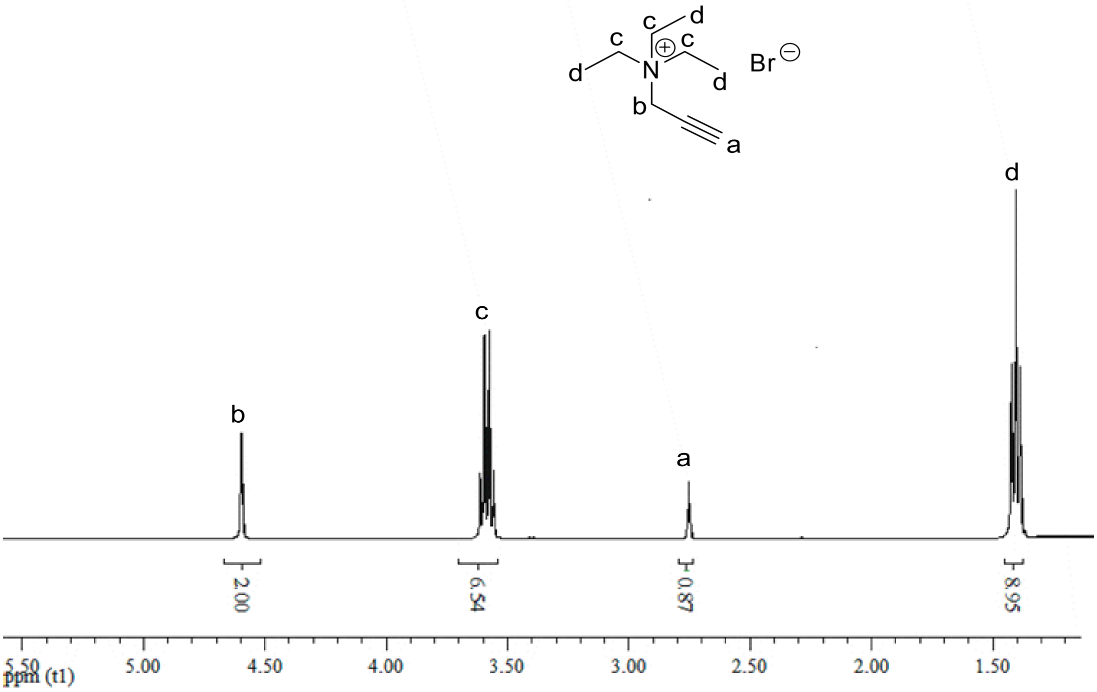
S6 ^{1}H- NMR spectrum of the alkyne containing IL **3a**.



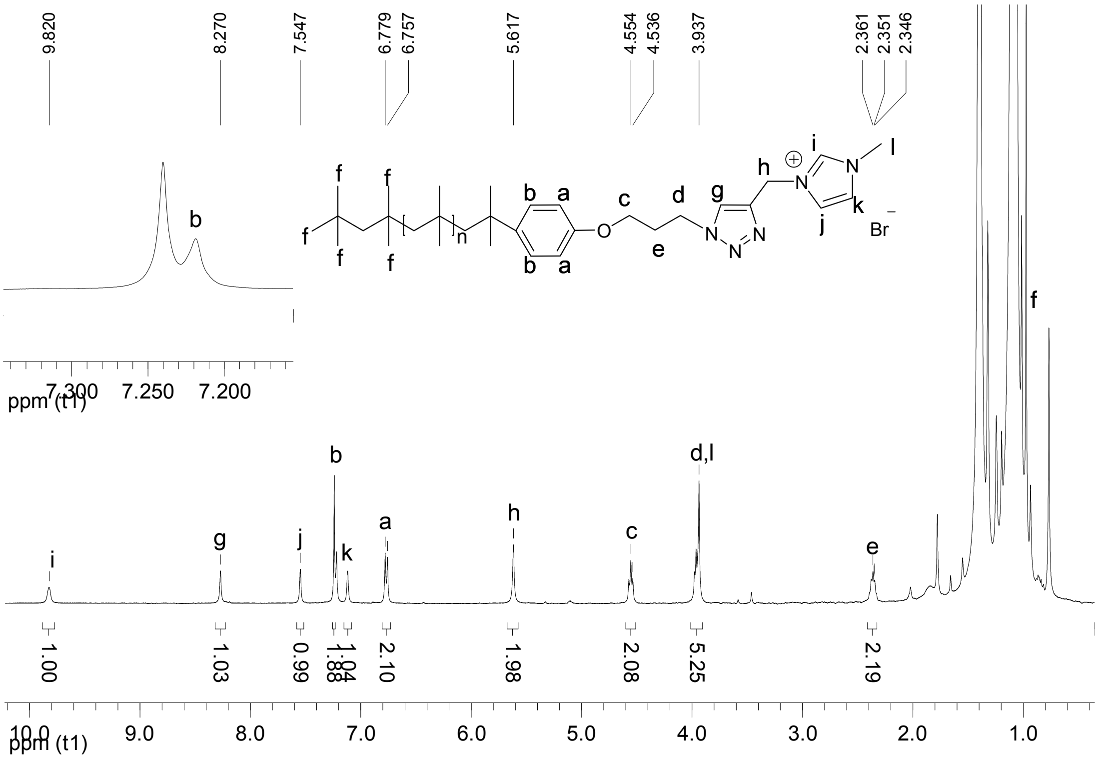
S7 ^{1}H- NMR spectrum of the alkyne containing IL **3b**.



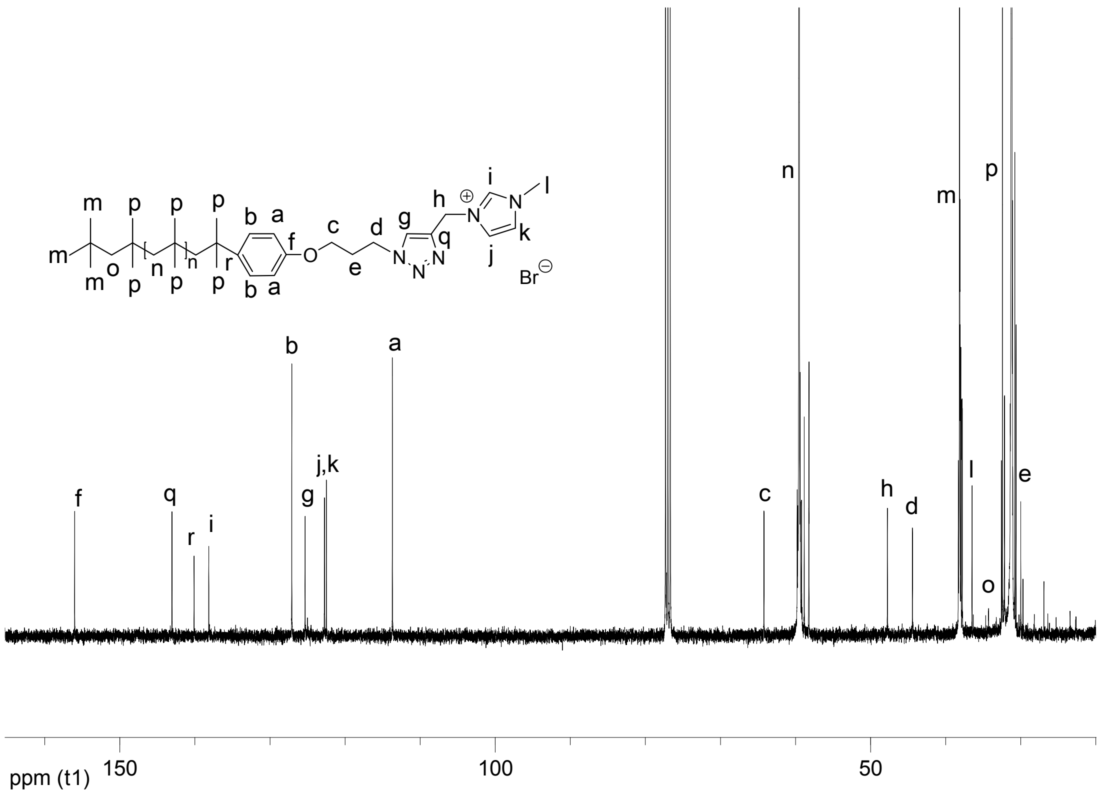
S8 ^{1}H- NMR spectrum of the alkyne containing IL **3c**.



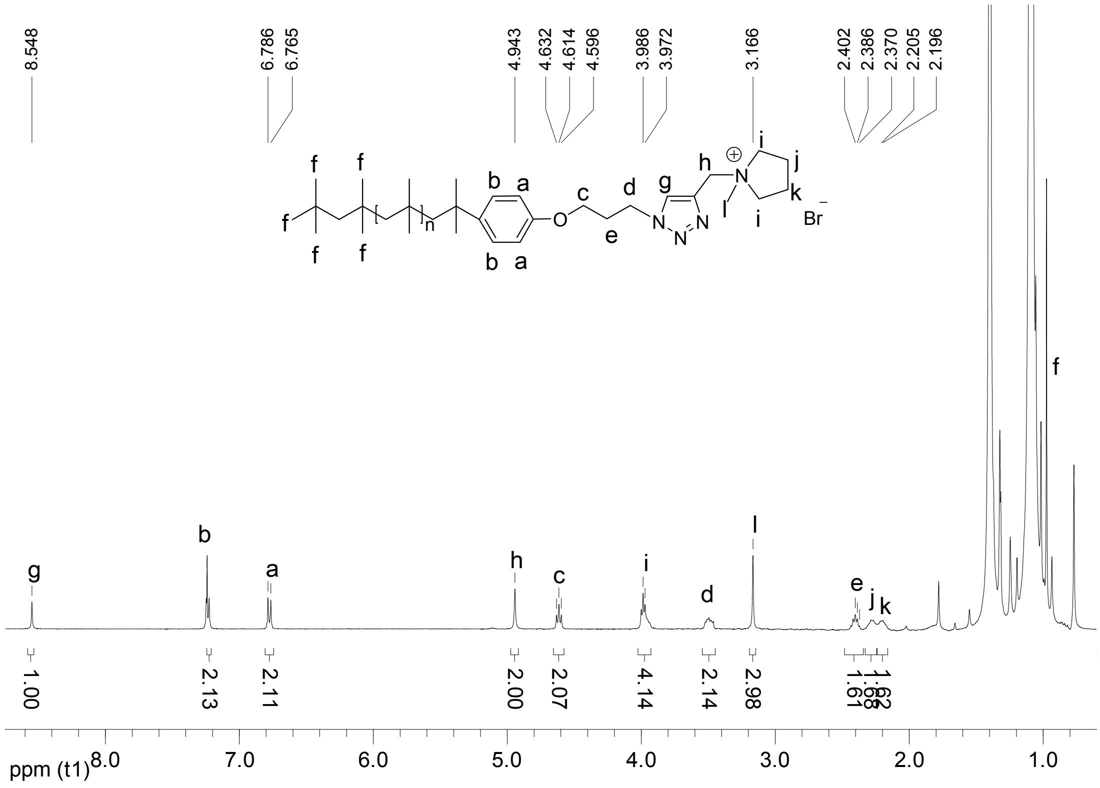
S9 ^{1}H-NMR spectrum of the 3-methyl-1-imidazolium telechelic PIB-IL **4a.**



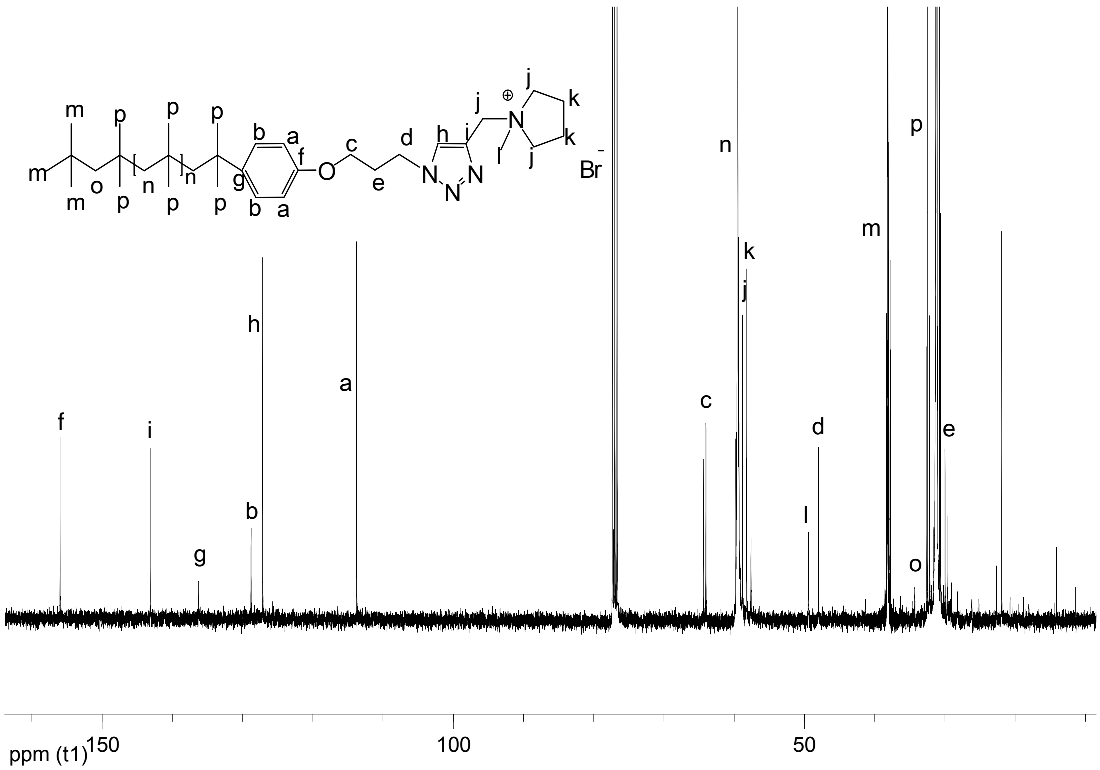
S10 ^{13}C-NMR spectrum of the 3-methyl-1-imidazolium telechelic PIB-IL **4a.**



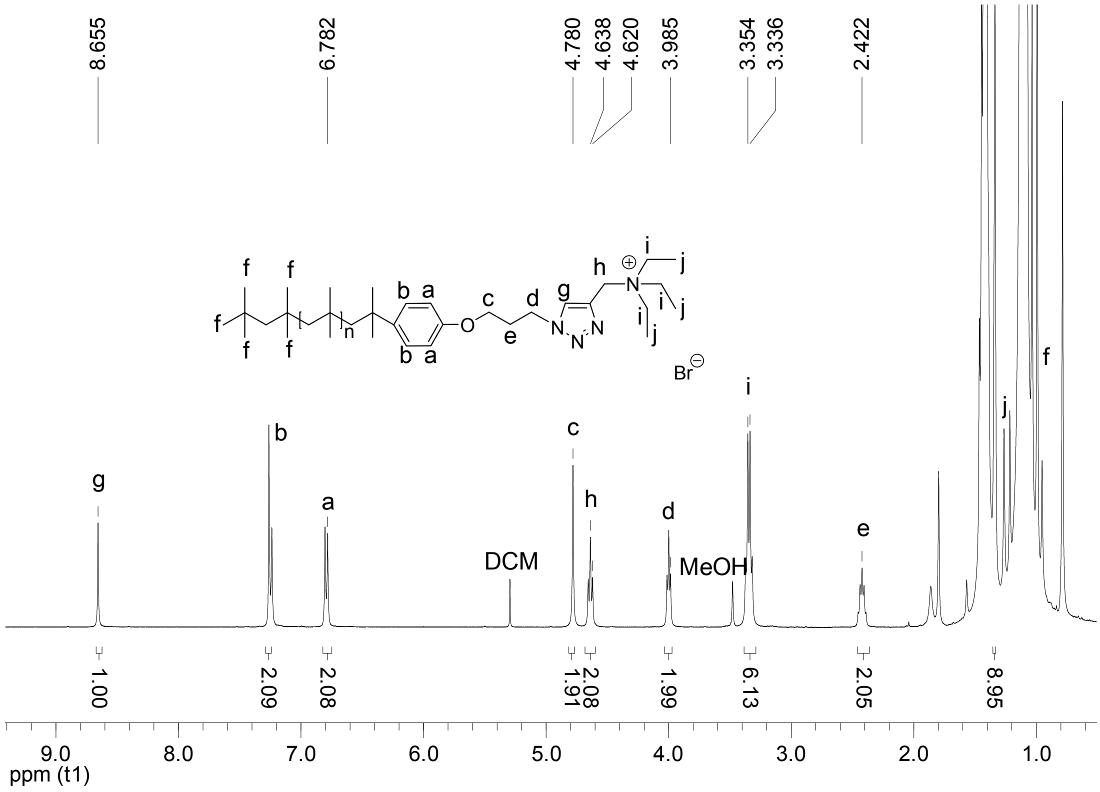
S11 ^{1}H-NMR spectrum of the 1-methylpyrrolidinium telechelic PIB-IL **4b.**



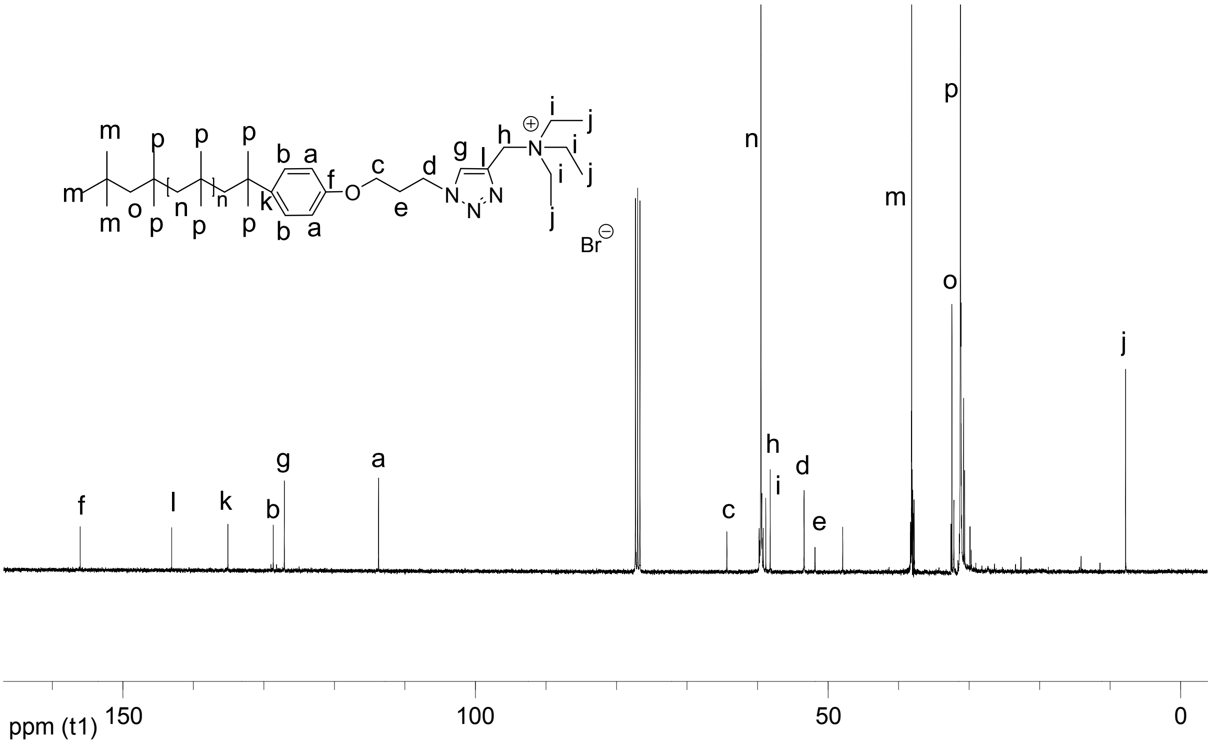
S12 ^{13}C-NMR spectrum of the 1-methylpyrrolidinium telechelic PIB-IL **4b.**



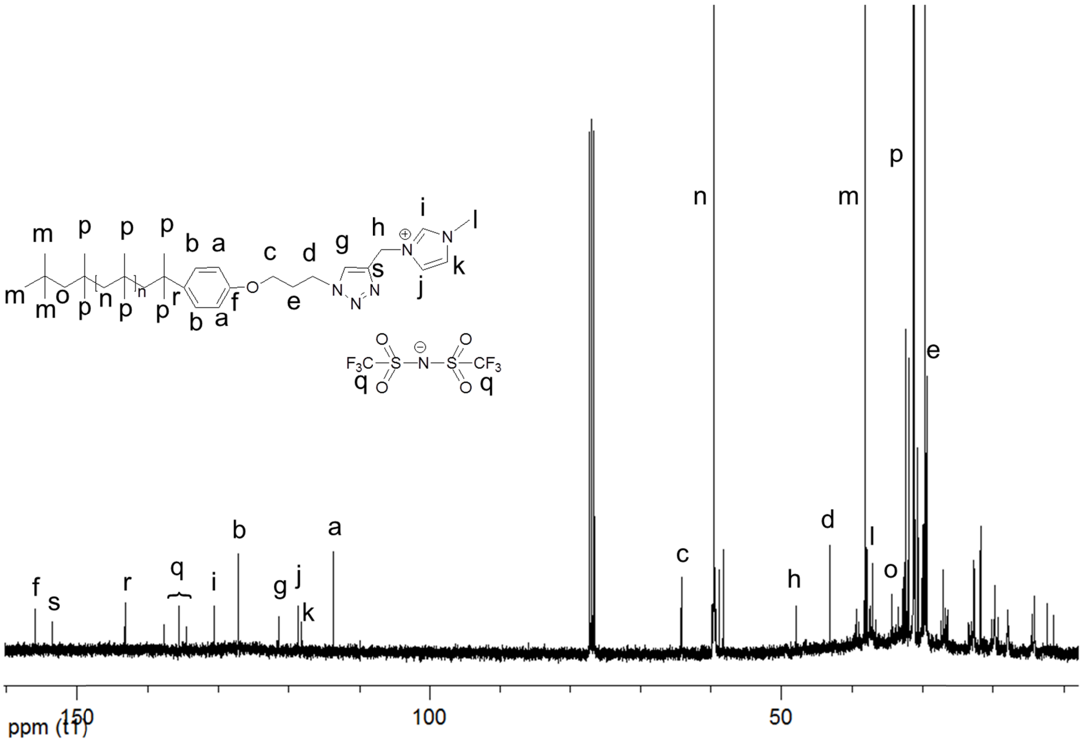
S13 ^{1}H-NMR spectrum of the *N,N,N*-triethylammonium telechelic PIB-IL **4a.**



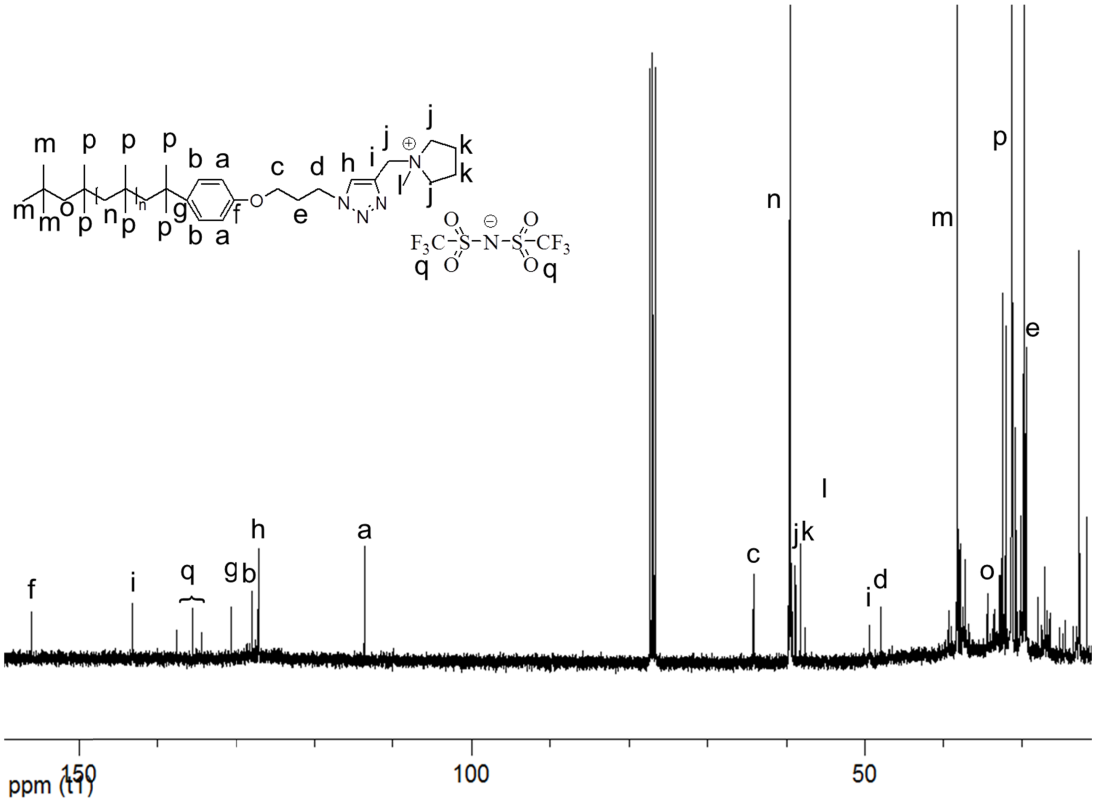
S14 ^{13}C-NMR spectrum of the *N,N,N*-triethylammonium telechelic PIB-IL **4c**



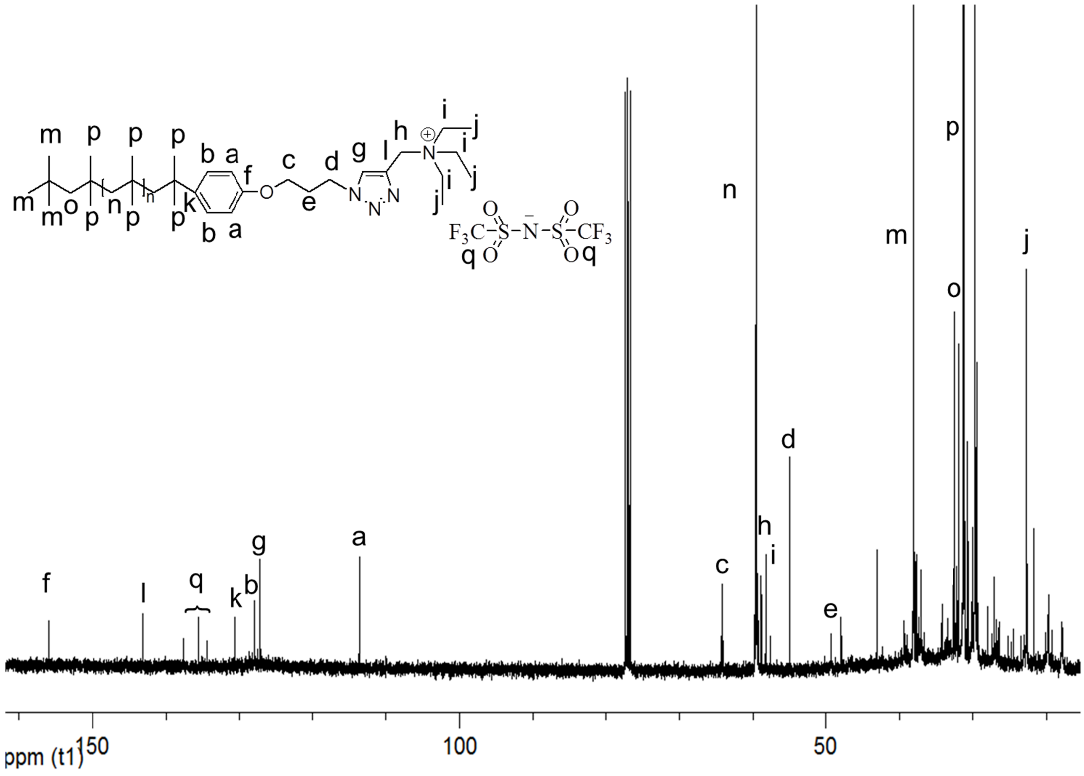
S15 ^{13}C-NMR spectrum of the 3-methyl-1-imidazolium PIB-IL **6a**



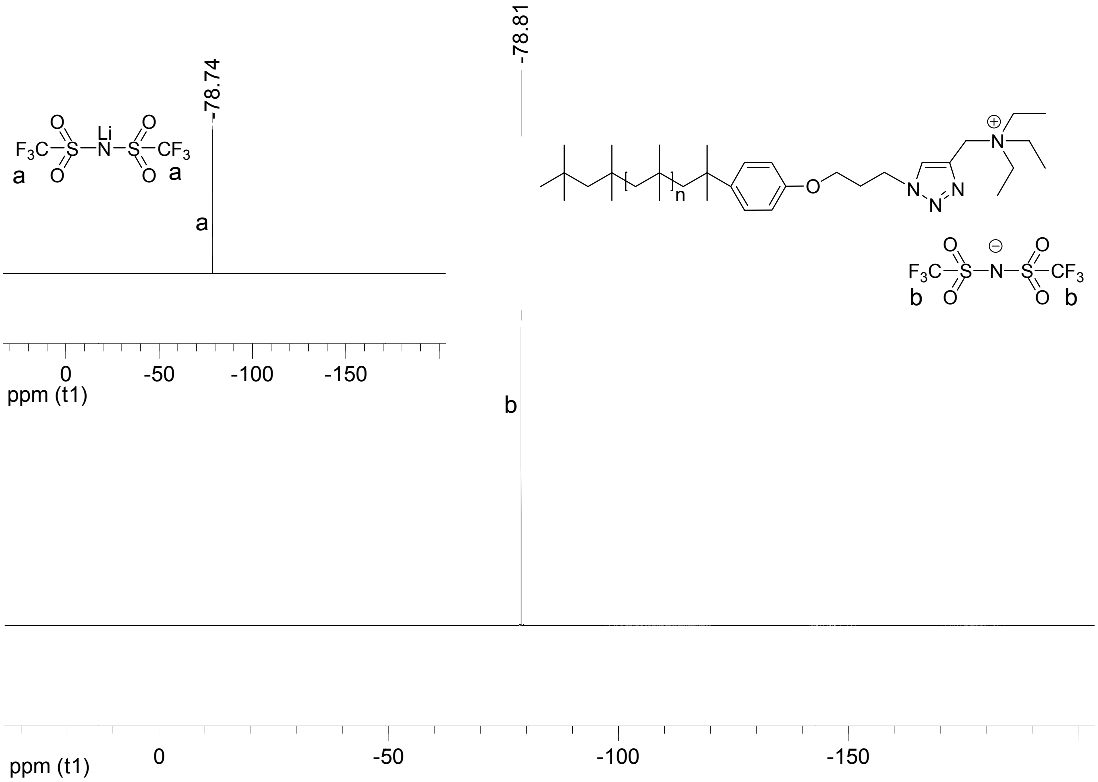
S16 ^{13}C-NMR spectrum of the 1-methylpyrrolidinium telechelic PIB-IL **6b**



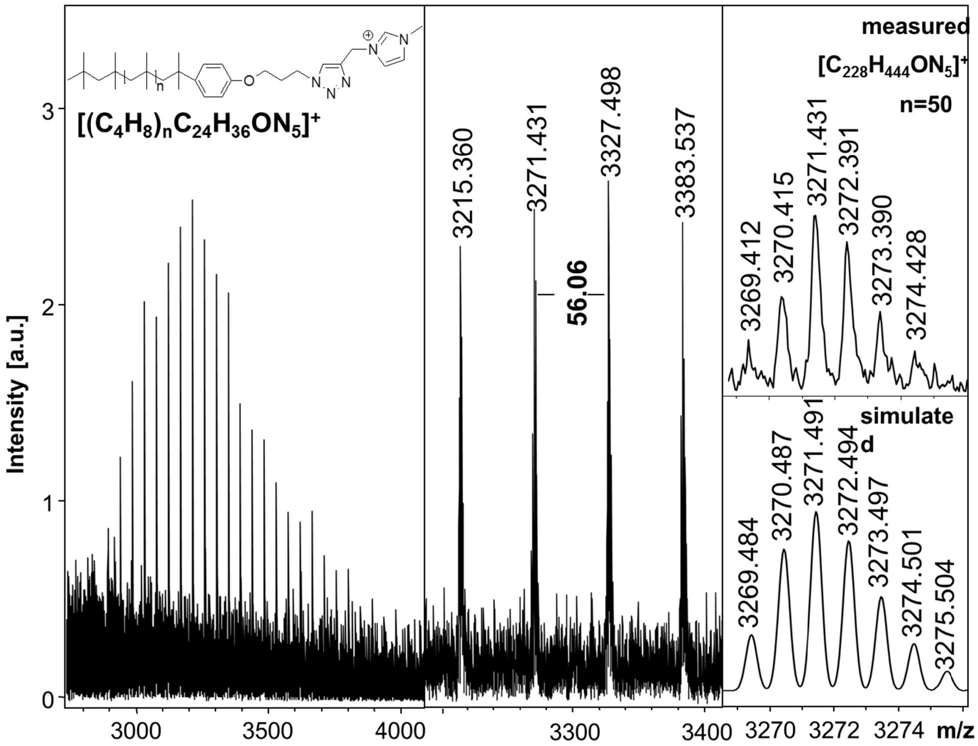
S17 ^{13}C-NMR spectrum of the *N,N,N*-triethylammonium telechelic PIB-IL **6c**



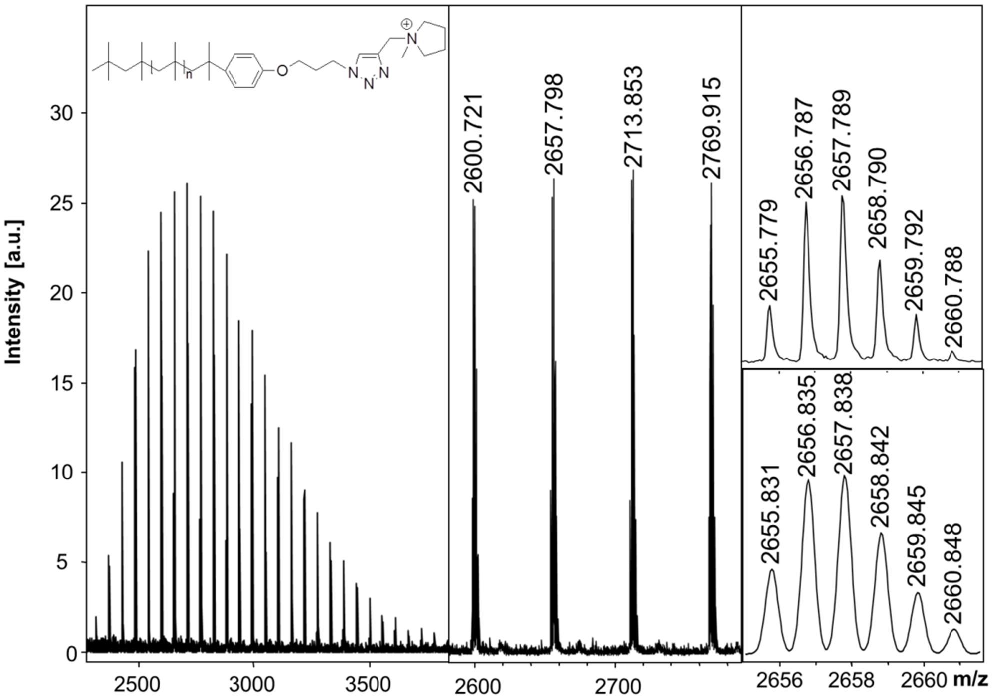
S18 ^{19}F-NMR spectrum of the *N,N,N*-triethylammonium telechelic PIB-IL **6c** and its corresponding lithium salt (signal a) for comparison



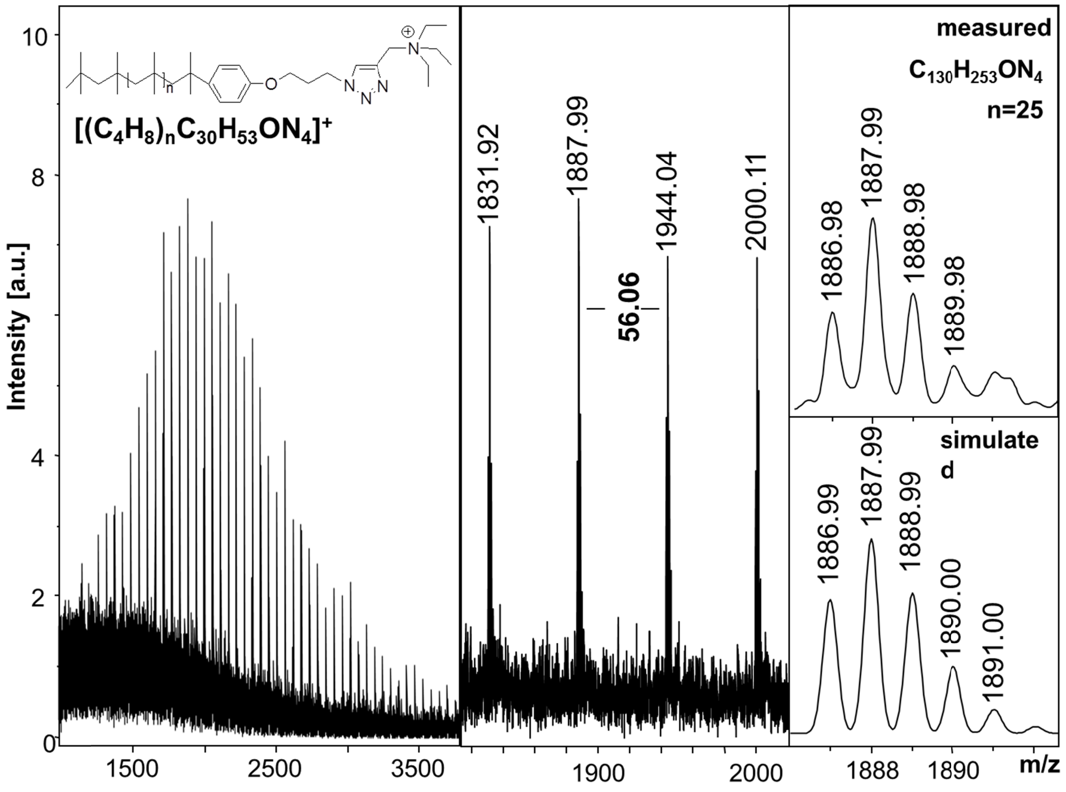
S19 MALDI-TOF-MS spectrum of the PIB-IL **6a**.



S20 MALDI-TOF-MS spectrum of the PIB-IL **6b**.

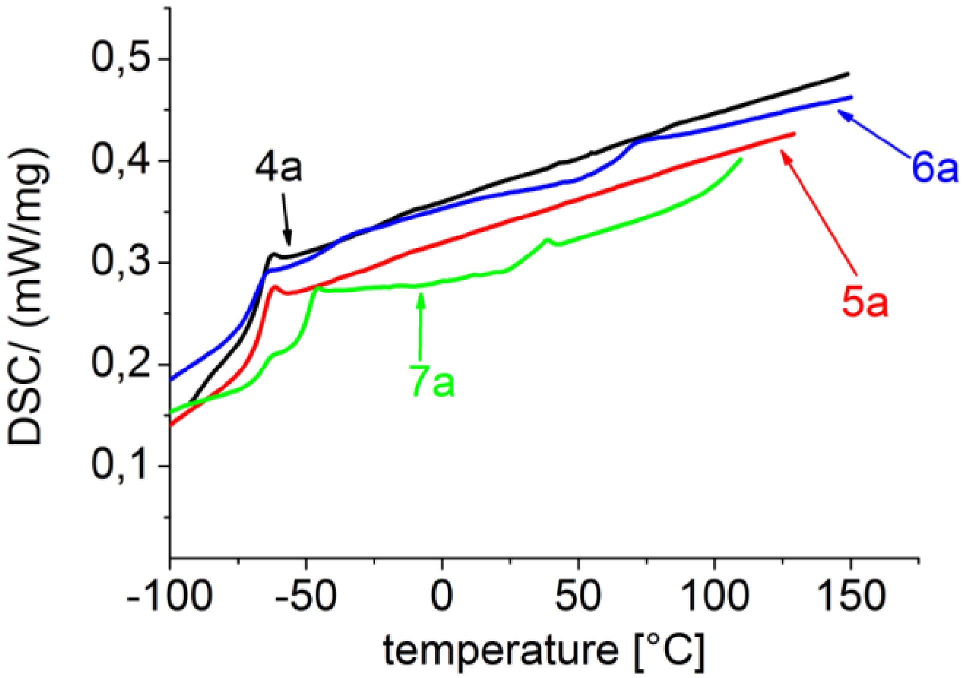


S21 MALDI-TOF-MS spectrum of the PIB-IL **6c**.

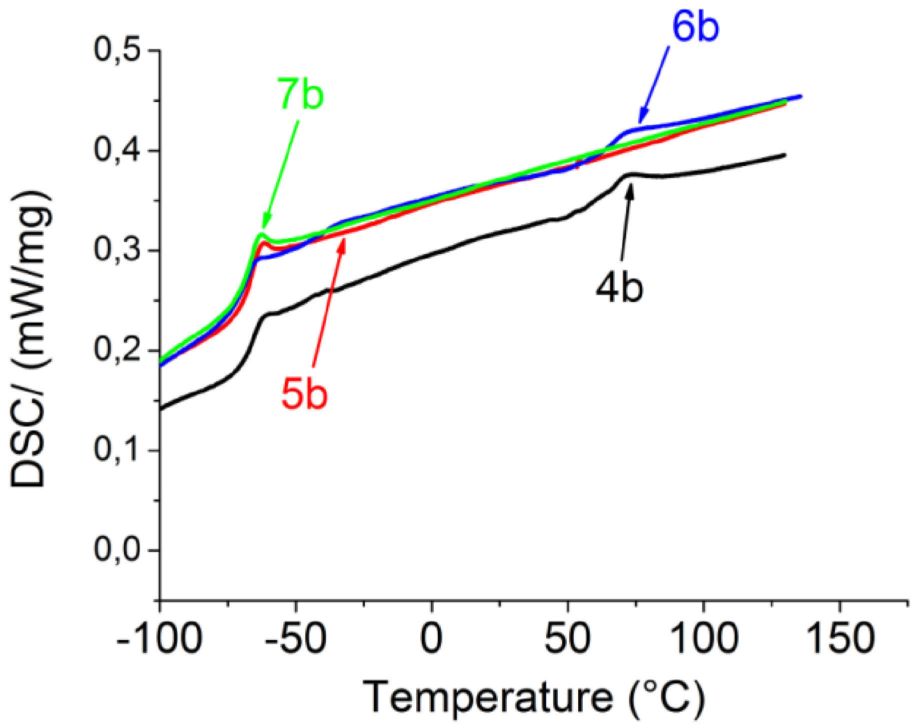


2. Thermal properties

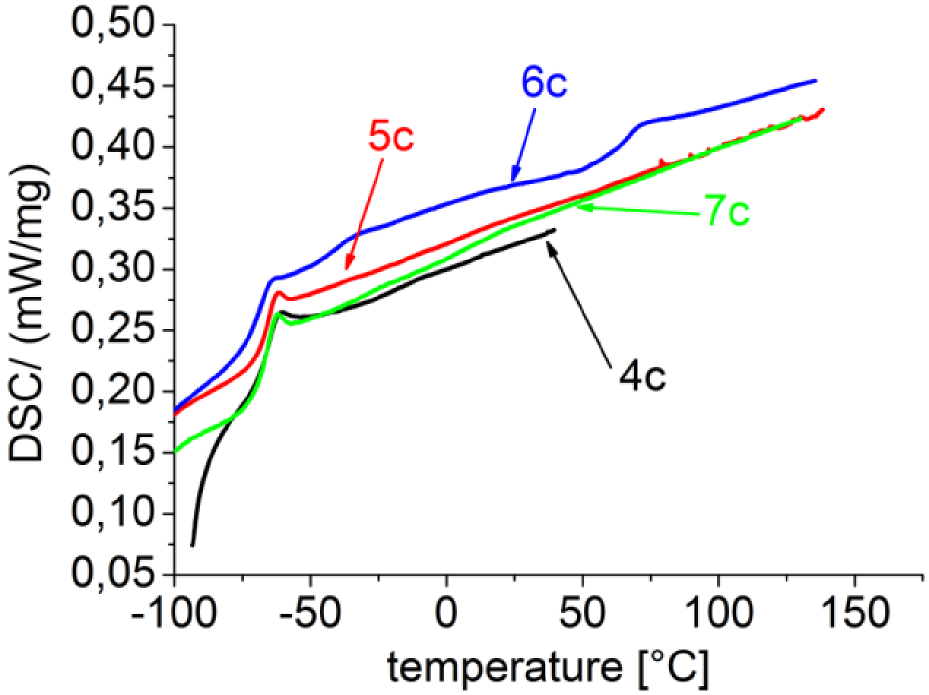
S22 DSC curves of the PIB-ILs **4-7a**



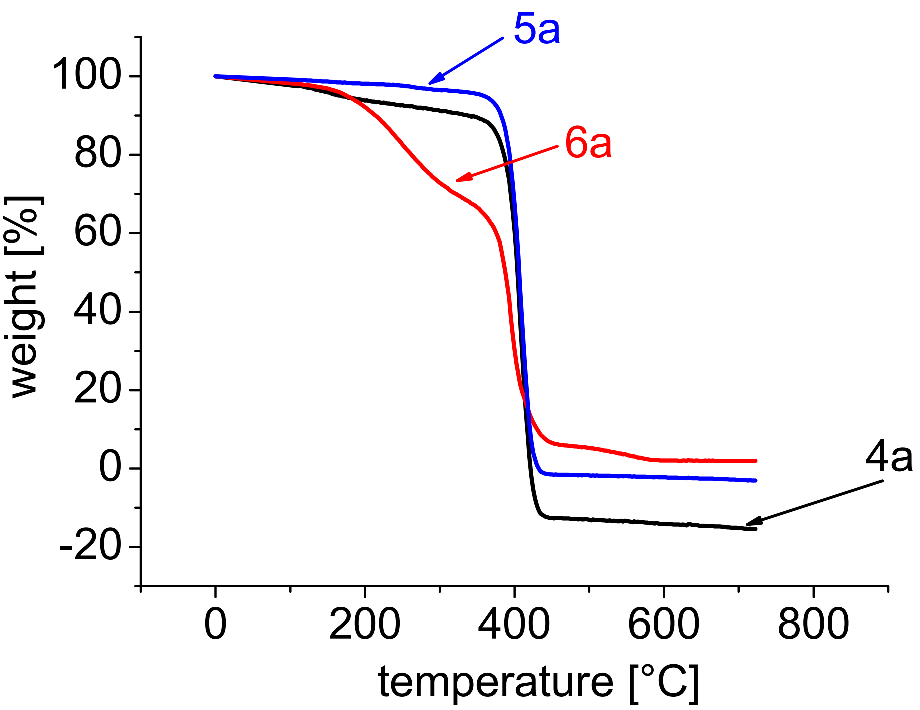
S23 DSC curves of the PIB-ILs **4-7b**



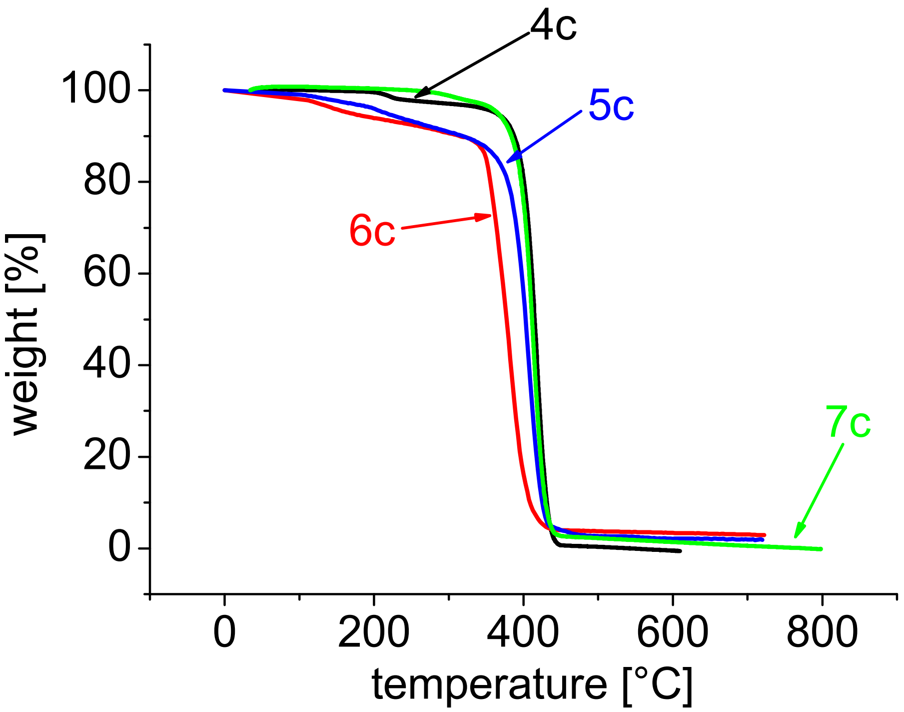
S24 DSC curves of the PIB-ILs **4-7c**



S25 TGA curves of the PIB-ILs **4-6a**

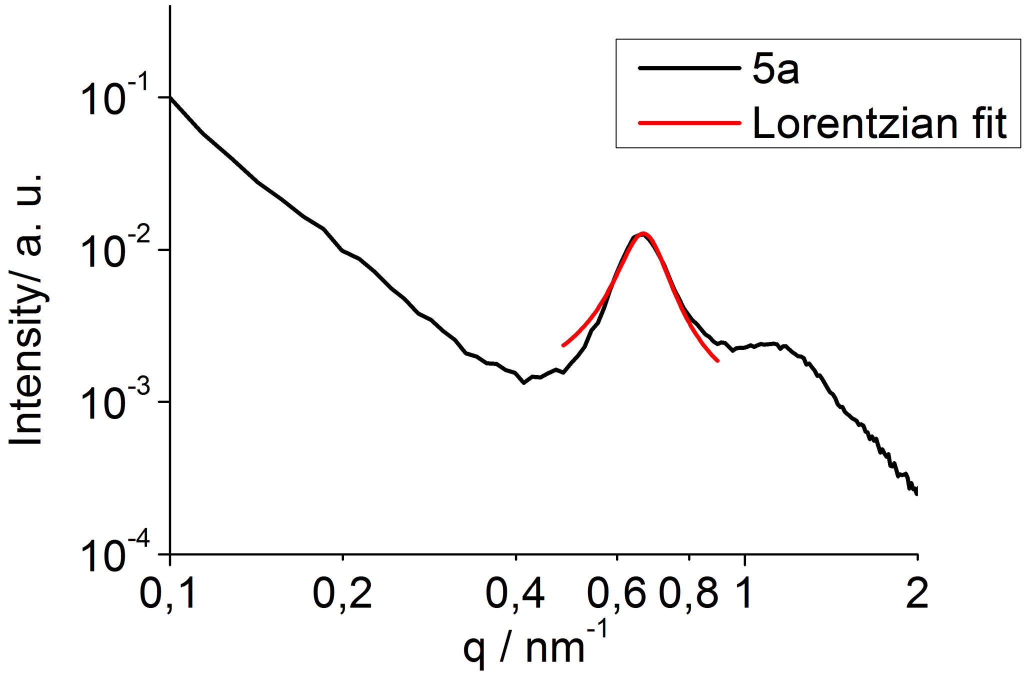


S26 TGA curves of the PIB-ILs **4-7c**

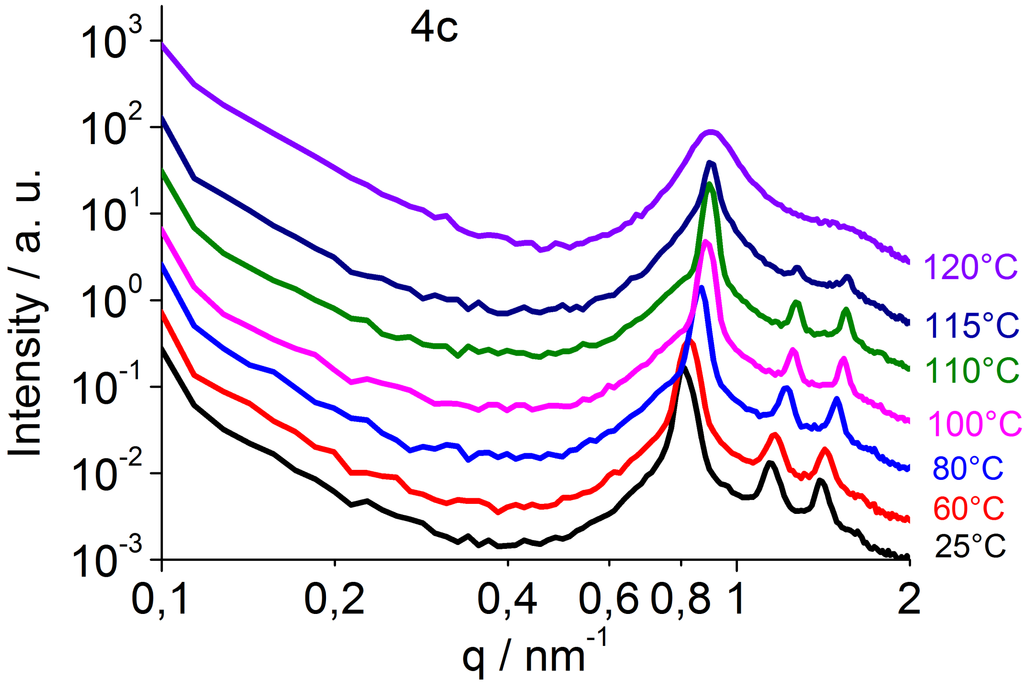


3. SAXS measurements

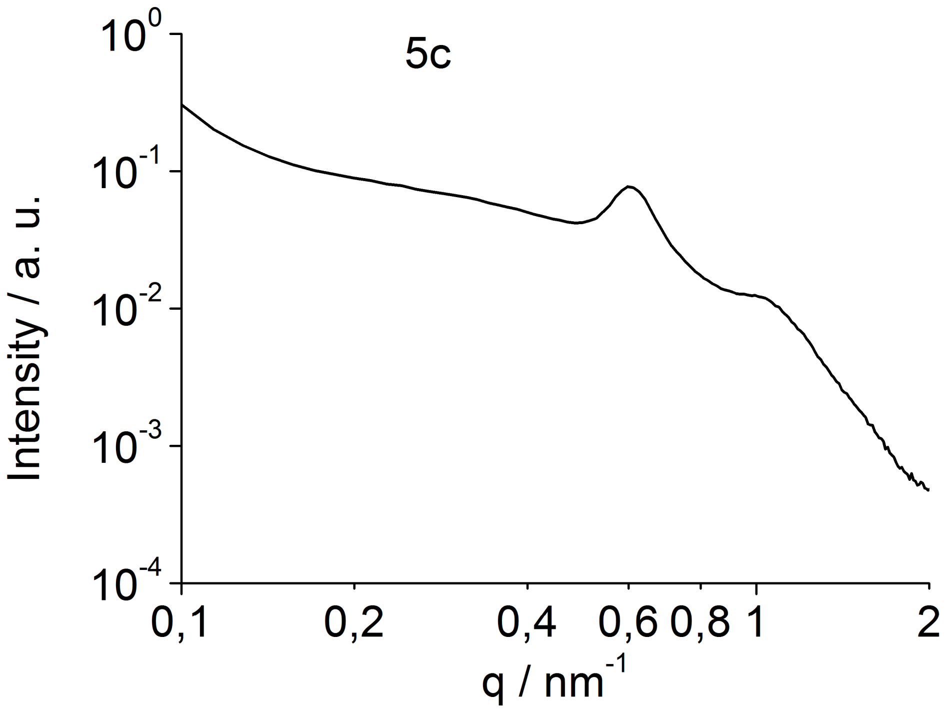
S27 Typical fit of a SAXS profile for the PIB-IL **5a** at room temperature with a Lorentzian curve.



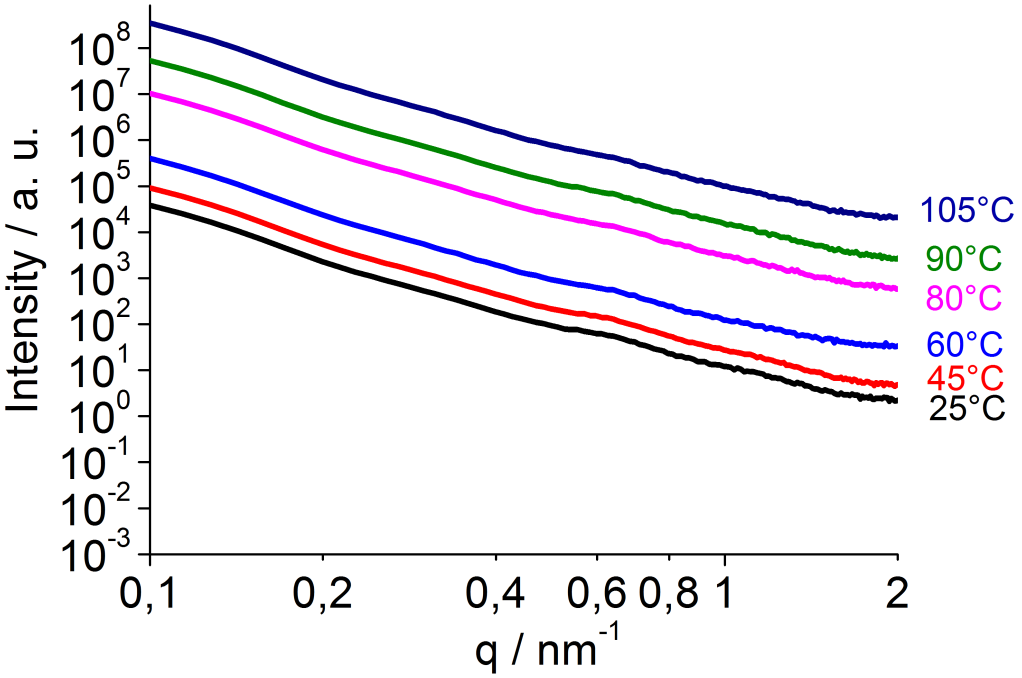
S28 *In-situ* SAXS profiles for the PIB-IL **4c**.



S29 SAXS profile for the PIB-IL **5c** at room temperature.

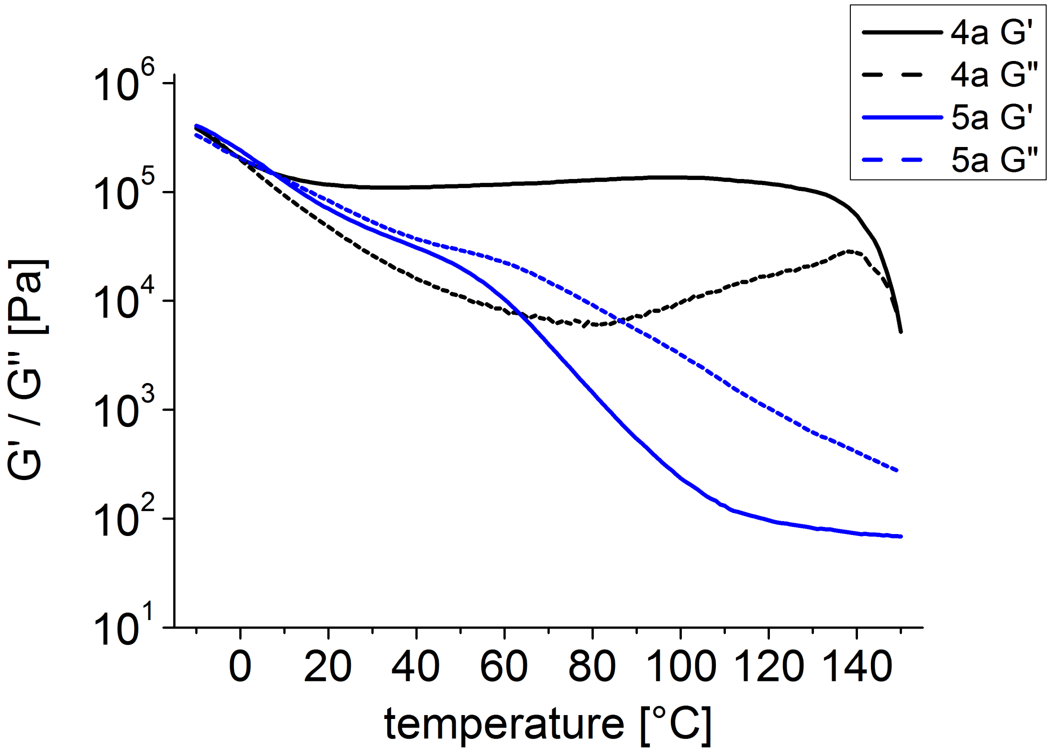


S30 *In-situ* SAXS profiles for the PIB-IL **7b**.

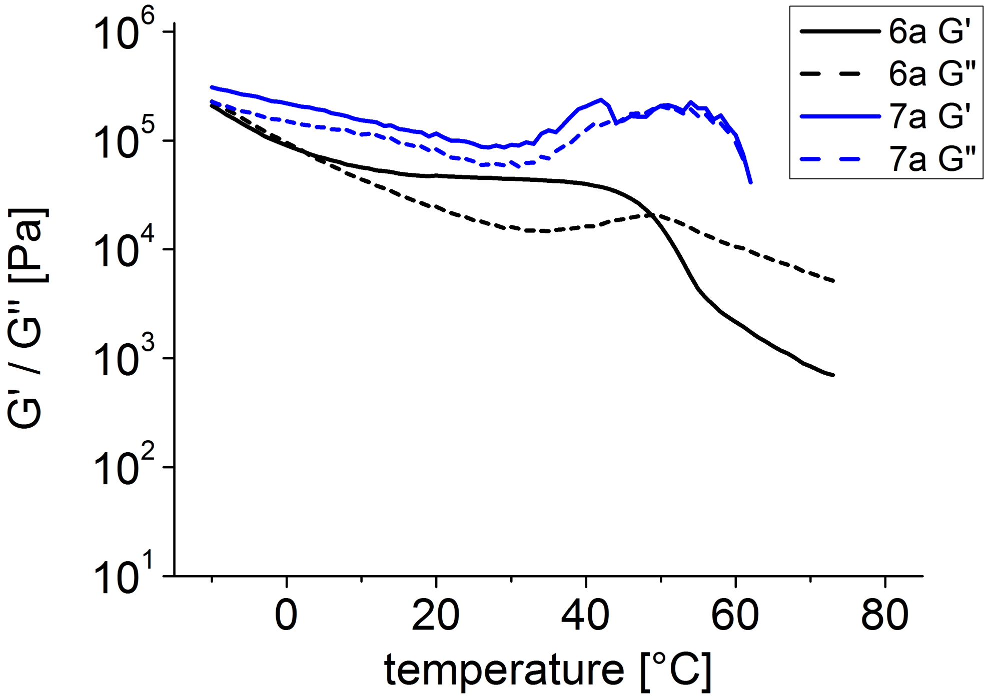


4. Rheology measurements

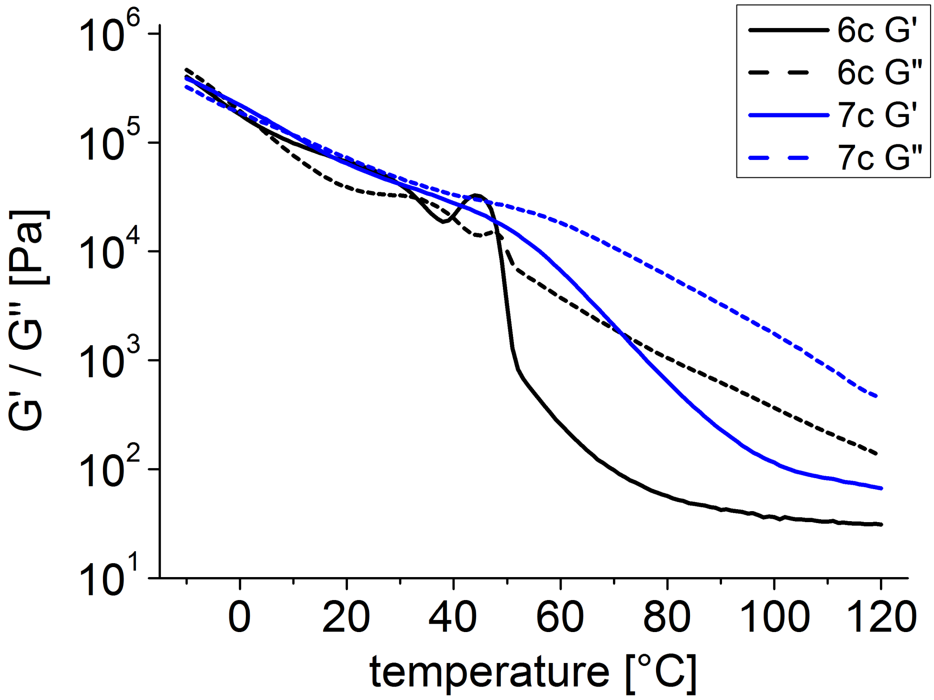
S31 Temperature-sweep measurements of the PIB-ILs **4a** and **5a**



S32 Temperature-sweep measurements of the PIB-ILs **6a** and **7a**



S33 Temperature-sweep measurements of the PIB-ILs **6c** and **7c**



1. D. L. Morgan and R. F. Storey, *Macromolecules*, 2009, **42**, 6844-6847.
2. P. Zare, A. Stojanovic, F. Herbst, J. Akbarzadeh, H. Peterlik and W. H. Binder, *Macromolecules*, 2012, **45**, 2074-2084.