Supporting information:

Chloroalkylsulfonate ionic liquids by ring opening of sultones with organic chloride salts

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1) Kinetics: Reaction of [BMIM]Cl with 1,4 butane sultone

The reaction was carried out in nitroethane. To determine the reaction order and the rate coefficient of this ring opening reaction, we used conditions of a pseudo first order reaction (large excess of one reactant). The reaction rate was determined using ^{1}H-NMR spectra of samples taken after different reaction times. Between sampling and NMR measurement all samples were kept at -10 °C. At this temperature all samples were solid as the applied NMR solvent d_6-DMSO has a melting point of 18°C. In this way we prevented the samples from further reaction during storage times that would have falsified the kinetic studies.

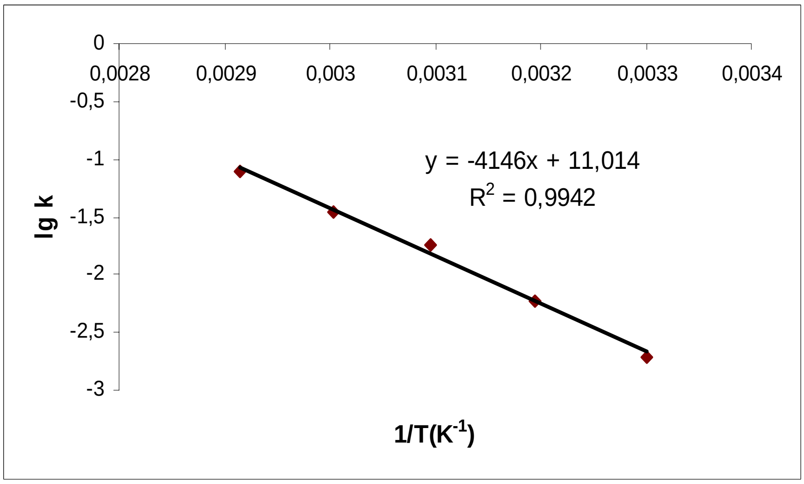
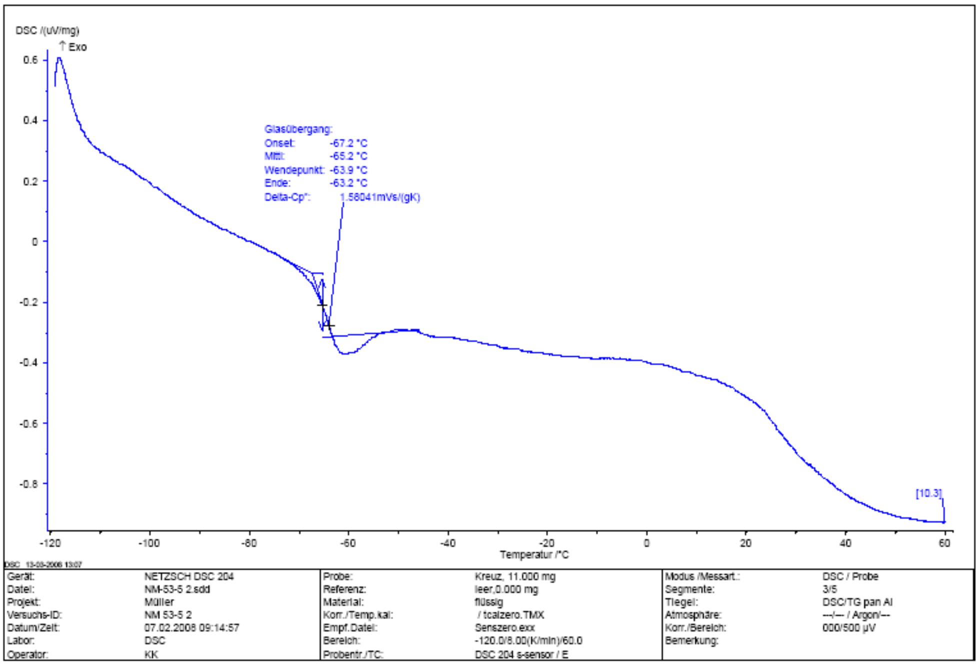


Figure S1: Arrhenius type plot for the reaction of [BMIM]Cl with 1,4-butane sultone to determine the activation energy of the ring opening reaction.

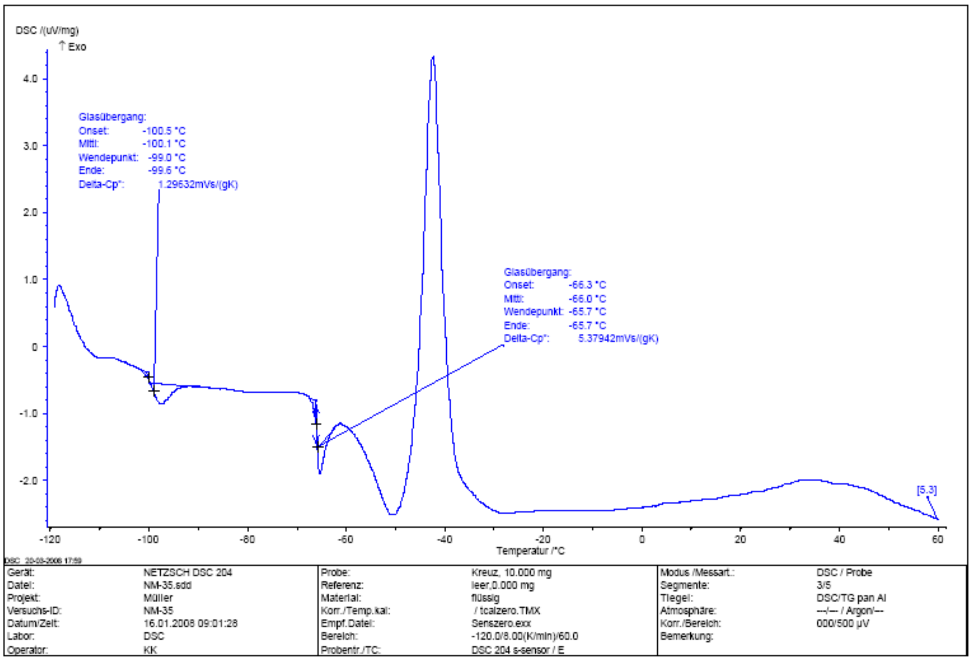
2) DSC measurements of ILs **3a-c**



Glasübergang:
Onset: -67.2 °C
Mittl: -65.2 °C
Wendepunkt: -63.9 °C
Ende: -63.2 °C
Delta-Cp*: 1.58041mVs/(gK)

Gerät:	NETZSCH DSC 204	Probe:	Kreuz, 11.000 mg	Modus /Messart.:	DSC / Probe
Datei:	NM-53-5 2.sdd	Referenz:	leer,0.000 mg	Segmente:	3/5
Projekt:	Müller	Material:	flüssig	Tiegel:	DSC/TG pan Al
Versuchs-ID:	NM 53-5 2	Korr./Temp.kal:	/ tcalzero.TMX	Atmosphäre:	---/--- / Argon/---
Datum/Zeit:	07.02.2008 09:14:57	Empf.Datei:	Senszero.exx	Korr./Bereich:	000/500 µV
Labor:	DSC	Bereich:	-120.0/8.00(K/min)/60.0	Bemerkung:	
Operator:	KK	Probentr./TC:	DSC 204 s-sensor / E		

Figure S2: DSC measurement for glass transition of **3a**

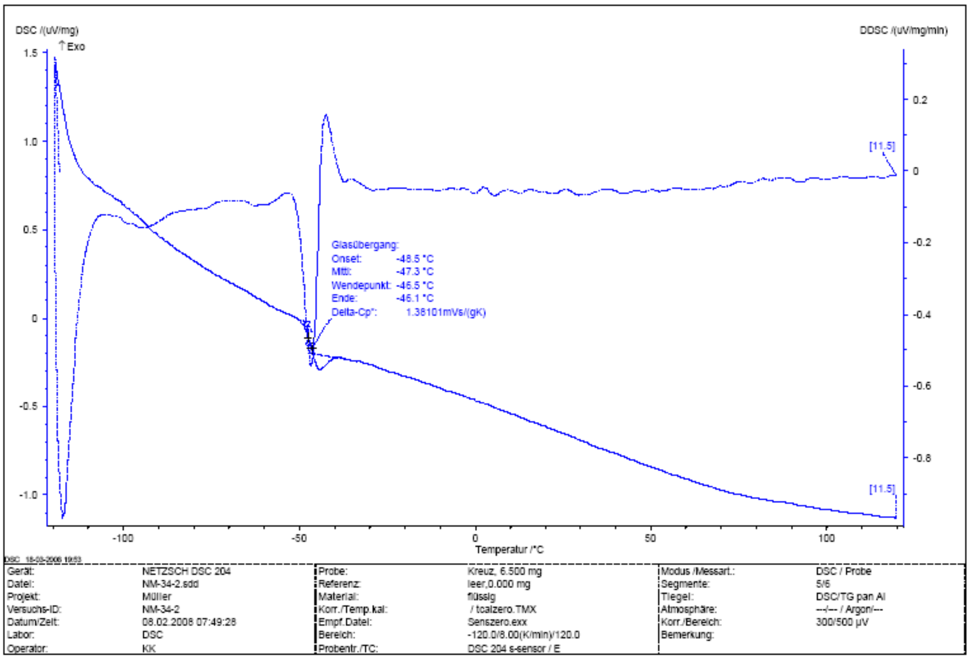


Glasübergang:
Onset: -100.5 °C
Mittl: -100.1 °C
Wendepunkt: -99.0 °C
Ende: -99.6 °C
Delta-Cp*: 1.29632mVs/(gK)

Glasübergang:
Onset: -66.3 °C
Mittl: -66.0 °C
Wendepunkt: -65.7 °C
Ende: -65.7 °C
Delta-Cp*: 5.37942mVs/(gK)

Gerät:	NETZSCH DSC 204	Probe:	Kreuz, 10.000 mg	Modus /Messart.:	DSC / Probe
Datei:	NM-35.sdd	Referenz:	leer,0.000 mg	Segmente:	3/5
Projekt:	Müller	Material:	flüssig	Tiegel:	DSC/TG pan Al
Versuchs-ID:	NM-35	Korr./Temp.kal:	/ tcalzero.TMX	Atmosphäre:	---/--- / Argon/---
Datum/Zeit:	16.01.2008 09:01:28	Empf.Datei:	Senszero.exx	Korr./Bereich:	000/500 µV
Labor:	DSC	Bereich:	-120.0/8.00(K/min)/60.0	Bemerkung:	
Operator:	KK	Probentr./TC:	DSC 204 s-sensor / E		

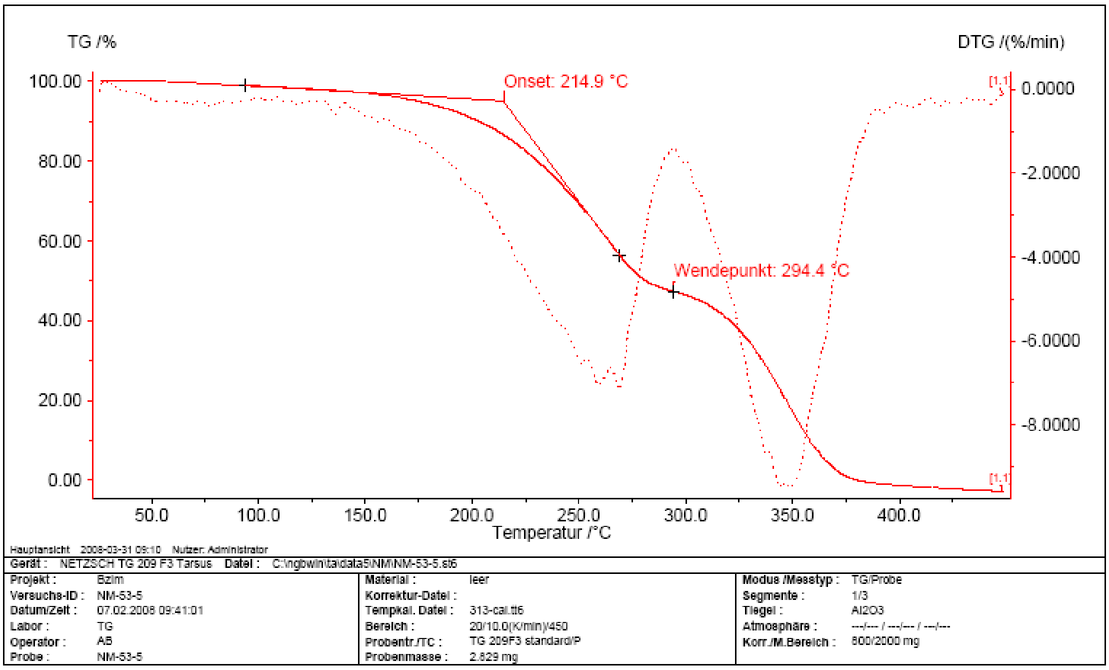
Figure S3: DSC measurement for glass transition of **3b**



Gerät:	NETZSCH DSC 204	Probe:	Kreuz, 6.500 mg	Modus /Messart.:	DSC / Probe
Datei:	NM-34-2.sdd	Referenz:	leer,0.000 mg	Segmente:	5/6
Projekt:	Müller	Material:	flüssig	Tiegel:	DSC/TG pan Al
Versuchs-ID:	NM-34-2	Korr./Temp.kal:	/ tcalzero.TMX	Atmosphäre:	---/--- / Argon/---
Datum/Zeit:	08.02.2008 07:49:28	Empf.Datei:	Senszero.exx	Korr./Bereich:	300/500 µV
Labor:	DSC	Bereich:	-120.0/8.00(K/min)/120.0	Bemerkung:	
Operator:	KK	Probentr./TC:	DSC 204 s-sensor / E		

Figure S4: DSC measurement for glass transition of **3c**

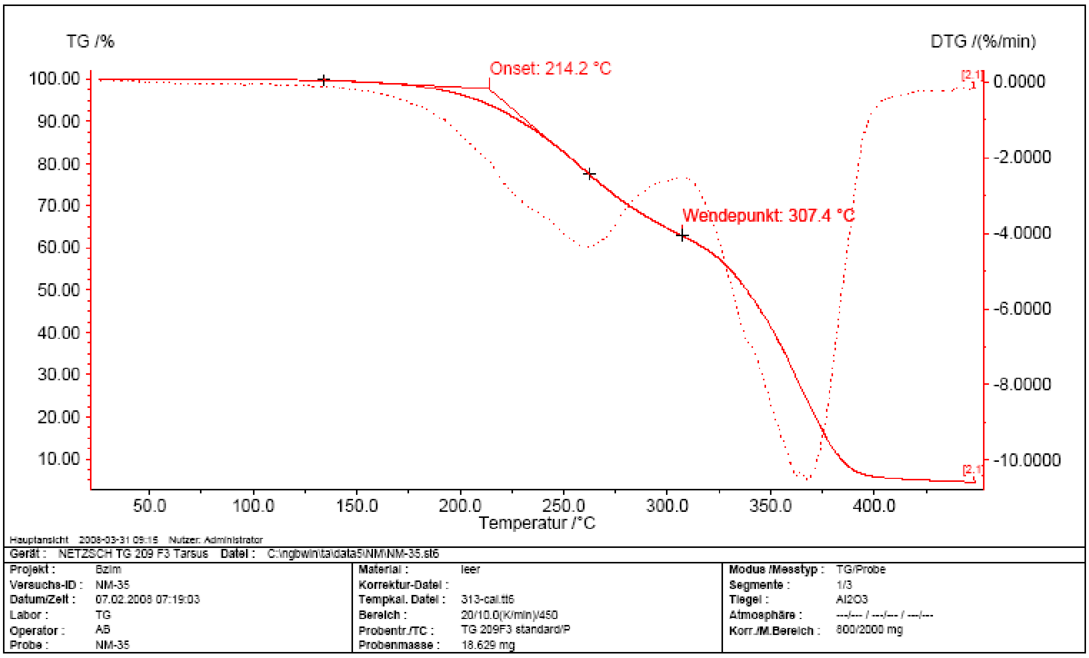
3) TGA analyses of ILs **3a-c**



Gerät : NETZSCH TG 209 F3 Tarsus Datei : C:\ngbwin\ta\data5\NM\NM-53-5.st6

Projekt :	Bzim	Material :	leer	Modus /Messtyp :	TG/Probe
Versuchs-ID :	NM-53-5	Korrektur-Datei :		Segmente :	1/3
Datum/Zeit :	07.02.2008 09:41:01	Tempkal. Datei :	313-cal.tt6	Tiegel :	Al2O3
Labor :	TG	Bereich :	20/10.0(K/min)/450	Atmosphäre :	---/--- / ---/--- / ---/---
Operator :	AB	Probentr./TC :	TG 209F3 standard/P	Korr./M.Bereich :	800/2000 mg
Probe :	NM-53-5	Probenmasse :	2.829 mg		

Figure S5: TGA-measurment of **3a** and their first derivation (dotted lines).



Hauptansicht 2008-03-31 09:15 Nutzer: Administrator

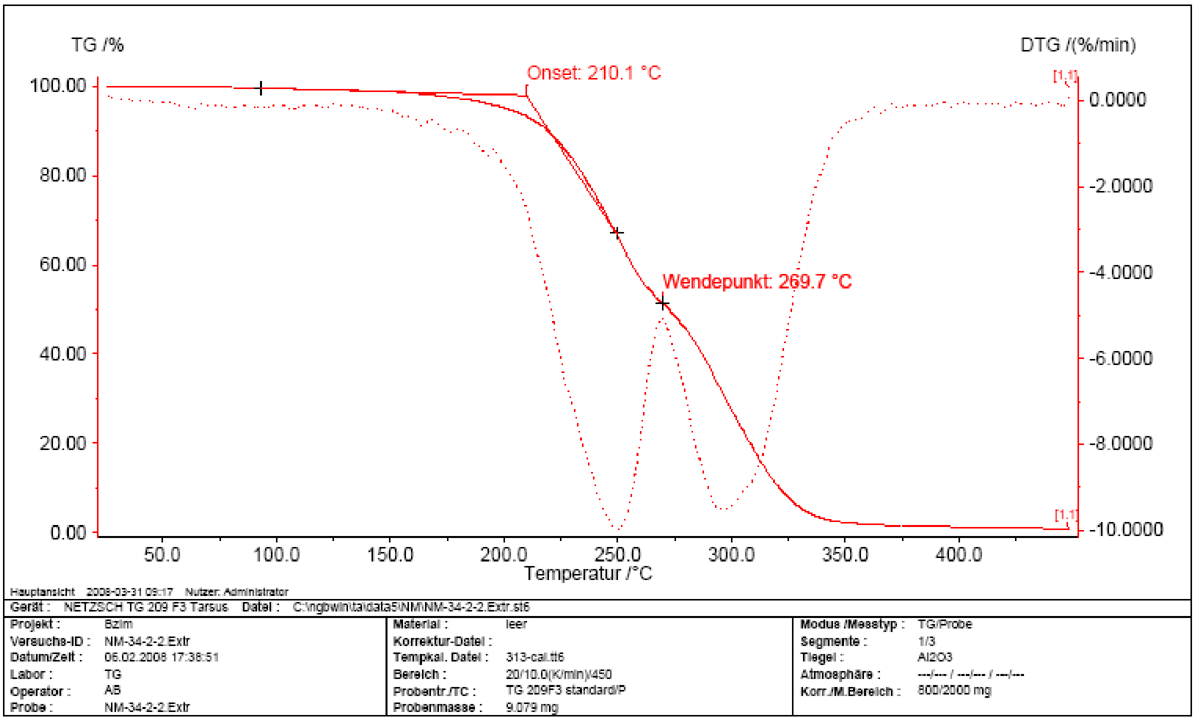
Gerät : NETZSCH TG 209 F3 Tarsus Datei : C:\ngbwin\ta\data5\NM\NM-35.st6

Projekt : Bzim
Versuchs-ID : NM-35
Datum/Zeit : 07.02.2008 07:19:03
Labor : TG
Operator : AB
Probe : NM-35

Material : leer
Korrektur-Datei :
Tempkal. Datei : 313-cal.tt6
Bereich : 20/10.0(K/min)/450
Probentr./TC : TG 209F3 standard/P
Probenmasse : 18.629 mg

Modus /Messtyp : TG/Probe
Segmente : 1/3
Tiegel : Al2O3
Atmosphäre : ---/--- / ---/--- / ---/---
Korr./M.Bereich : 800/2000 mg

Figure S6: TGA-measurment of **3b** and their first derivation (dotted lines).



Hauptansicht 2008-03-31 09:17 Nutzer: Administrator

Gerät : NETZSCH TG 209 F3 Tarsus Datei : C:\ngbwin\ta\data5\NM\NM-34-2-2.Extr.st6

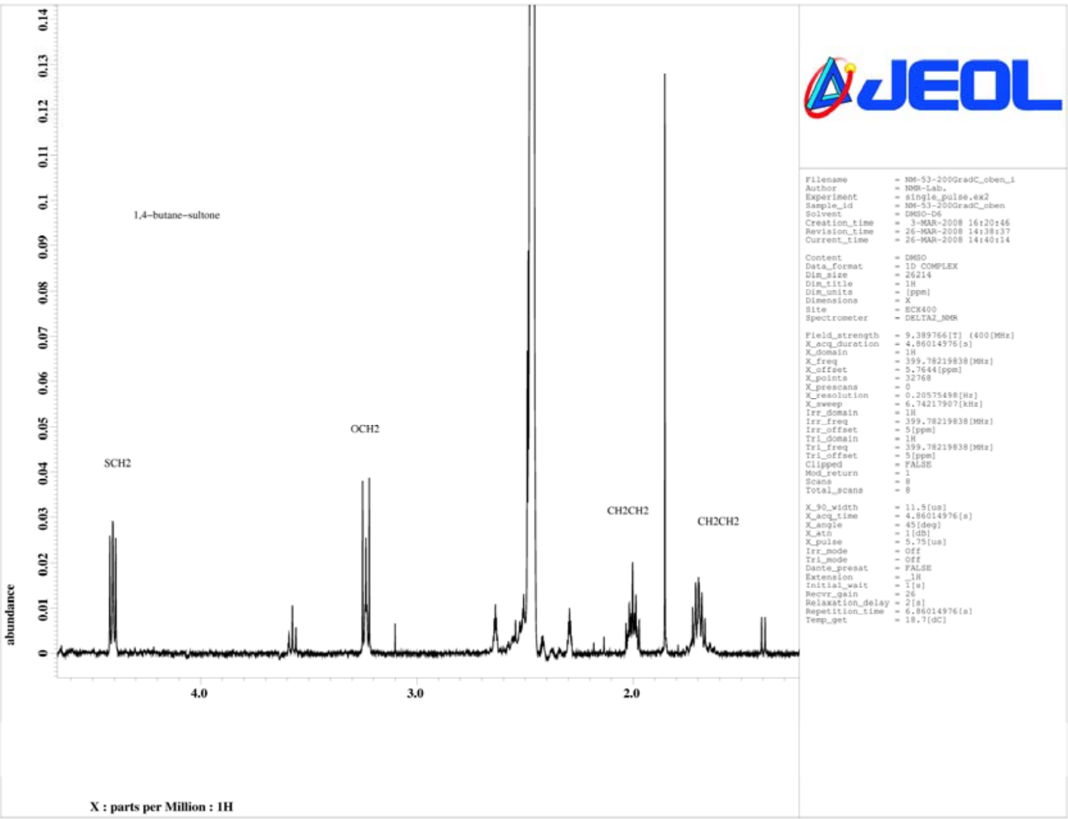
Projekt : Bzim
Versuchs-ID : NM-34-2-2.Extr
Datum/Zeit : 06.02.2008 17:38:51
Labor : TG
Operator : AB
Probe : NM-34-2-2.Extr

Material : leer
Korrektur-Datei :
Tempkal. Datei : 313-cal.tt6
Bereich : 20/10.0(K/min)/450
Probentr./TC : TG 209F3 standard/P
Probenmasse : 9.079 mg

Modus /Messtyp : TG/Probe
Segmente : 1/3
Tiegel : Al2O3
Atmosphäre : ---/--- / ---/--- / ---/---
Korr./M.Bereich : 800/2000 mg

Figure S7: TGA-measurment of **3c** and their first derivation (dotted lines).

4) NMR analyses after treating **3a** for 4h at 210°C in an open system



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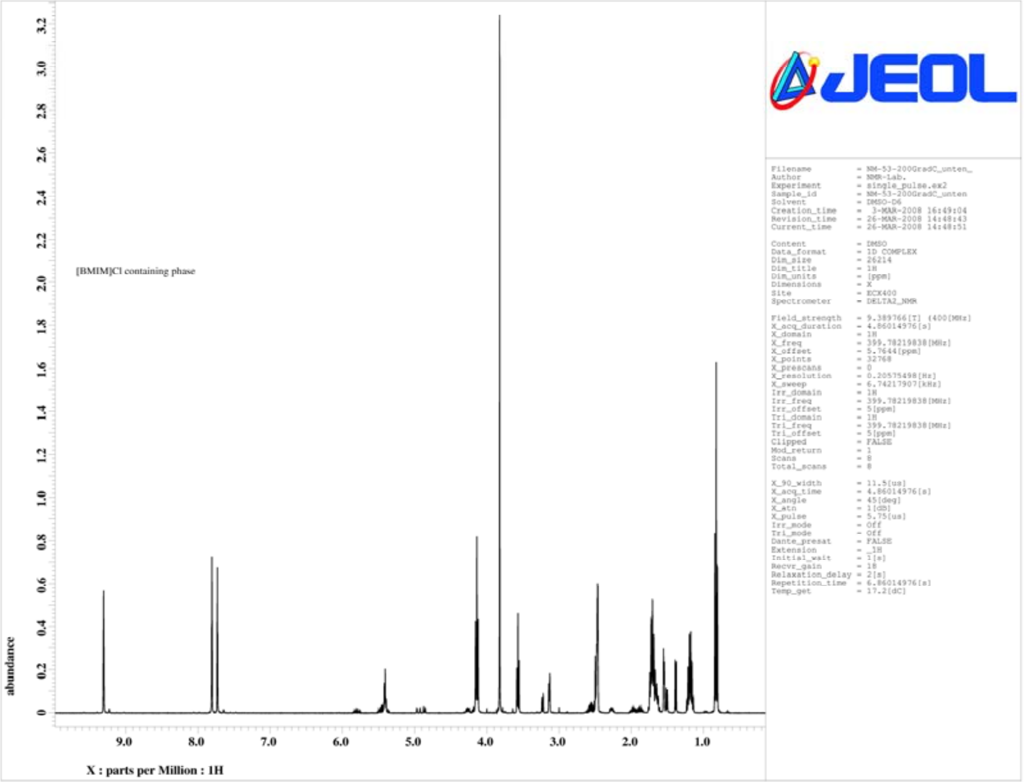
Filename           = NM-53-200GradC_oben_i
Author             = NMR-Lab.
Experiment         = single_pulse.ex2
Sample_id          = NM-53-200GradC_oben
Solvent            = DMSO-D6
Creation_time      =  3-MAR-2008 16:20:46
Revision_time      = 26-MAR-2008 14:38:37
Current_time       = 26-MAR-2008 14:40:14

Content            = DMSO
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX400
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.86014976[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5.7644[ppm]
X_points           = 32768
X_prescans         = 0
X_resolution       = 0.20575498[Hz]
X_sweep            = 6.74217907[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 8
Total_scans        = 8

X_90_width         = 11.5[us]
X_acq_time         = 4.86014976[s]
X_angle            = 45[deg]
X_atn              = 1[dB]
X_pulse            = 5.75[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Extension          = _1H
Initial_wait       = 1[s]
Recvr_gain         = 26
Relaxation_delay   = 2[s]
Repetition_time    = 6.86014976[s]
Temp_get           = 18.7[dC]
```

Figure S8: ^{1}H-NMR spectra of evaporated fraction after thermal decomposition of **3a**.



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Filename           = NM-53-200GradC_unten_
Author             = NMR-Lab.
Experiment         = single_pulse.ex2
Sample_id          = NM-53-200GradC_unten
Solvent            = DMSO-D6
Creation_time      =  3-MAR-2008 16:49:04
Revision_time      = 26-MAR-2008 14:48:43
Current_time       = 26-MAR-2008 14:48:51

Content            = DMSO
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX400
Spectrometer       = DELTA2_NMR

Field_strength     = 9.389766[T] (400[MHz]
X_acq_duration     = 4.86014976[s]
X_domain           = 1H
X_freq             = 399.78219838[MHz]
X_offset           = 5.7644[ppm]
X_points           = 32768
X_prescans         = 0
X_resolution       = 0.20575498[Hz]
X_sweep            = 6.74217907[kHz]
Irr_domain         = 1H
Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 399.78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 8
Total_scans        = 8

X_90_width         = 11.5[us]
X_acq_time         = 4.86014976[s]
X_angle            = 45[deg]
X_atn              = 1[dB]
X_pulse            = 5.75[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Extension          = _1H
Initial_wait       = 1[s]
Recvr_gain         = 18
Relaxation_delay   = 2[s]
Repetition_time    = 6.86014976[s]
Temp_get           = 17.2[dC]
```

Figure S9: ^{1}H-NMR spectra of remaining fraction after thermal decomposition of **3a**.

5) XPS analysis and elevated temperature (330 K)

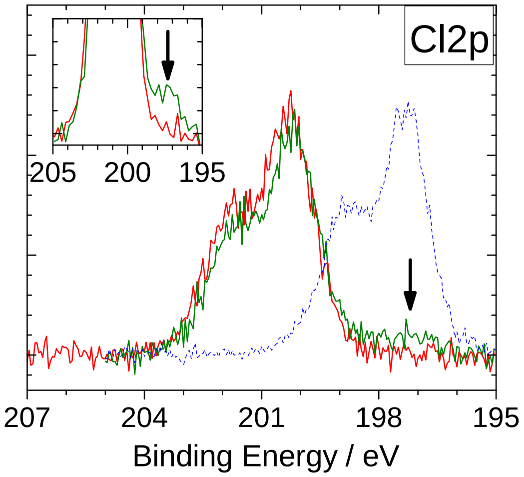

Figure S10: XP spectra of **3a** ([BMIM][$ClC_4H_8SO_3$]) in the Cl2p region taken at 70° emission angle at the beginning (red) and after several hours of XP measurements (green) at various temperatures (RT, 270 K and 330 K). The latter exhibit a growing shoulder at about 197 eV binding energy (see also inset) which is the typical position of chloride. The chloride spectrum of [EMIM]Cl (blue) is added for comparison.

6) Instruments:

NMR-Spectra were measured on a JEOL ECX 400 spectrometer.

XPS was performed with an ESCALAB 200 system with Al K_α source ($h\nu = 1486.6$ eV) and overall energy resolution of 0.9 eV. The Au $4f_{7/2}$ signal ($E_B = 83.55$ eV) was used as a reference for the reported binding energies. The detection limit of XPS of the near surface composition is in the order of 0.5 - 5 atom% (depending on XPS cross sections of the probed core level).

Elemental analysis were measured on an Euro EA 3000 (Euro Vector) and EA 1108 (Carlo Erba)

MALDI ToF mass spectrometry

Mass spectrometrical analysis was performed on a MALDI CFR^{plus} (AXIMA, Kratos Analytical, UK), equipped with a nitrogen laser (337 nm, 3 ns pulse, maximum pulse rate 10 Hz) at 1.9 µJ.