Supporting Information

Crosslinked Xylose-Based Polyester as a Bio-Derived Solid Polymer Electrolyte for Li^+-Ion Conduction

Matthew Oshinowo, James R. Runge, Marco Piccini, Frank Marken and Antoine Buchard*

Department of Chemistry, Centre for Sustainable and Circular Technologies, University of Bath, Claverton Down, Bath BA2 7AY, UK

Email: a.buchard@bath.ac.uk

Contents

1. Calculation of theoretical molar mass

The theoretical molar mass ($M_{n,theo}$) of poly(**1**) was determined using a version of the Carothers equation:

$$M_{\mathrm{n,theo}} = \mathrm{MW}_{\mathrm{repeat\ unit}} \times \left(\frac{(1 + \mathrm{r})}{(1 + \mathrm{r}) - (2 \times \mathrm{r}) \times \mathrm{conv.}}\right) \quad \textbf{(Equation 1)}$$

$$\mathrm{r} = \left(\frac{n_{\mathbf{1}}}{n_{\mathbf{1}} + 2(n_{\mathrm{cat}} + n_{\mathrm{mod}})}\right) \quad \textbf{(Equation 2)}$$

where $n_{\mathbf{1}}$ is the number of moles of monomer **1**, n_{cat} is the number of moles of G-II or HG-II, and n_{mod} is the number of moles of methyl 10-undecenoate.

2. NMR spectra

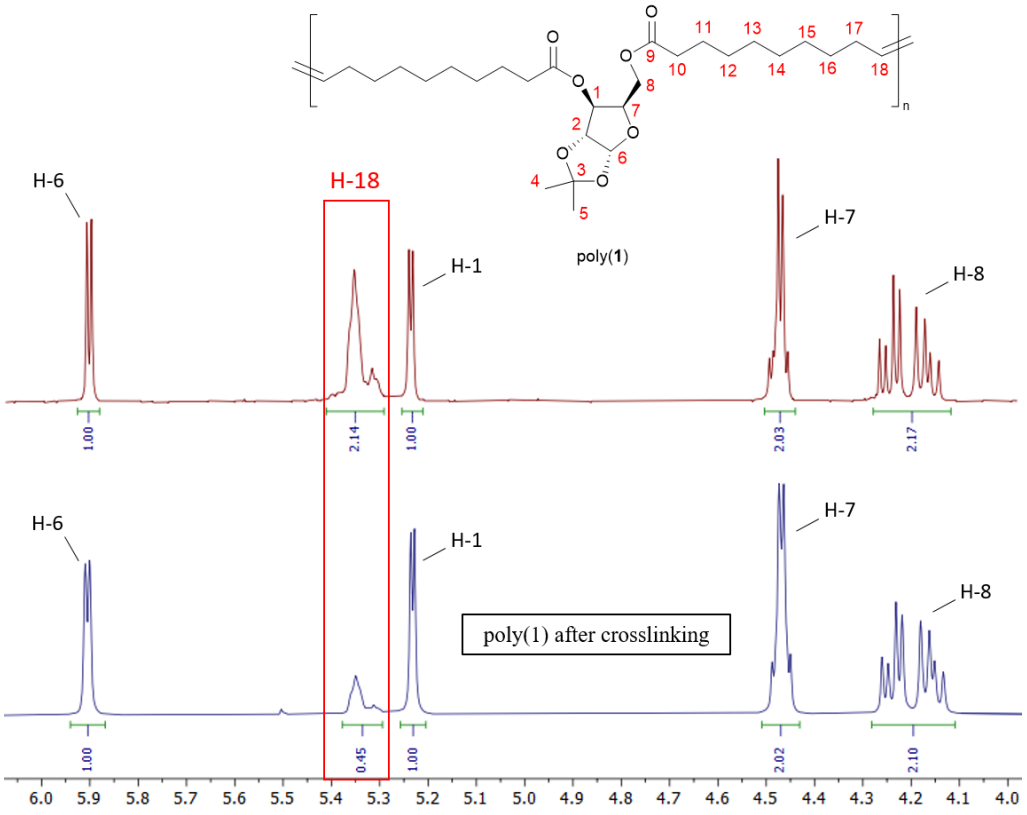


Fig. S1: Zoomed in ^{1}H NMR spectra of poly(**1**) in $CDCl_3$ before and after crosslinking with an excess (10 equivalents) of EDDET (neat, 2 hours, 70 °C, 365 nm).

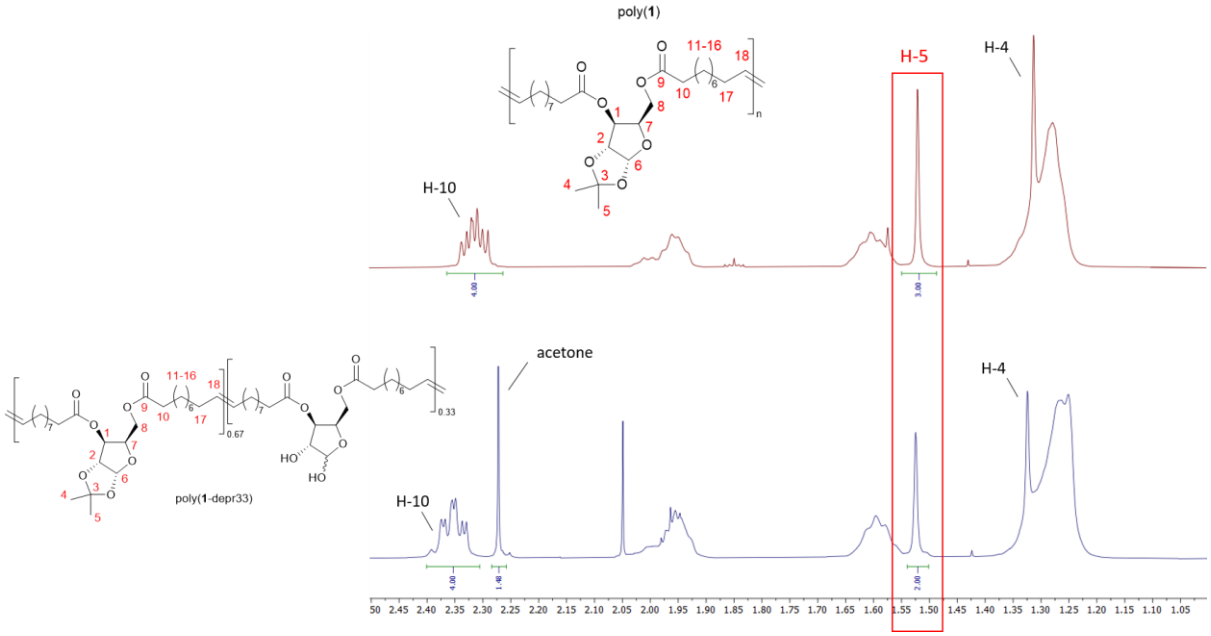


Fig. S2: Zoomed in ^{1}H NMR spectra of poly(**1**) and poly(**1**-depr33) in $CDCl_3$ showing the reduction in relative integration of the isopropylidene methyl peak upon deprotection of OH group. Acetone peak is present as the by-product of OH deprotection.

3. FTIR spectra

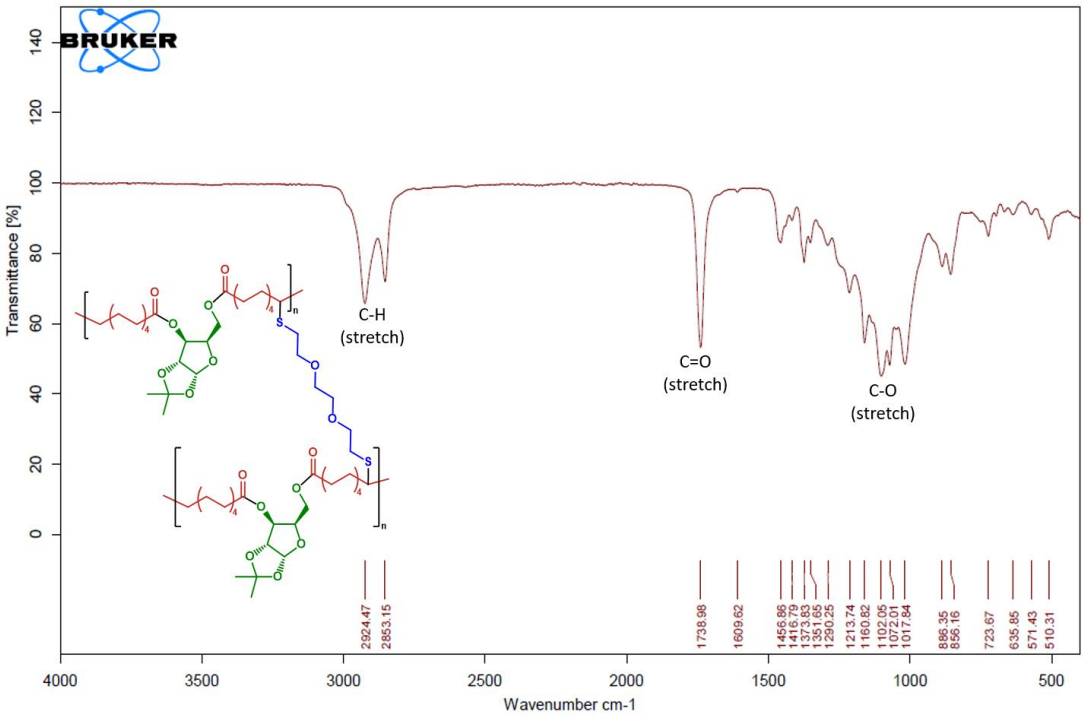


Fig. S3: FTIR spectrum of poly(**1**-EDDET).

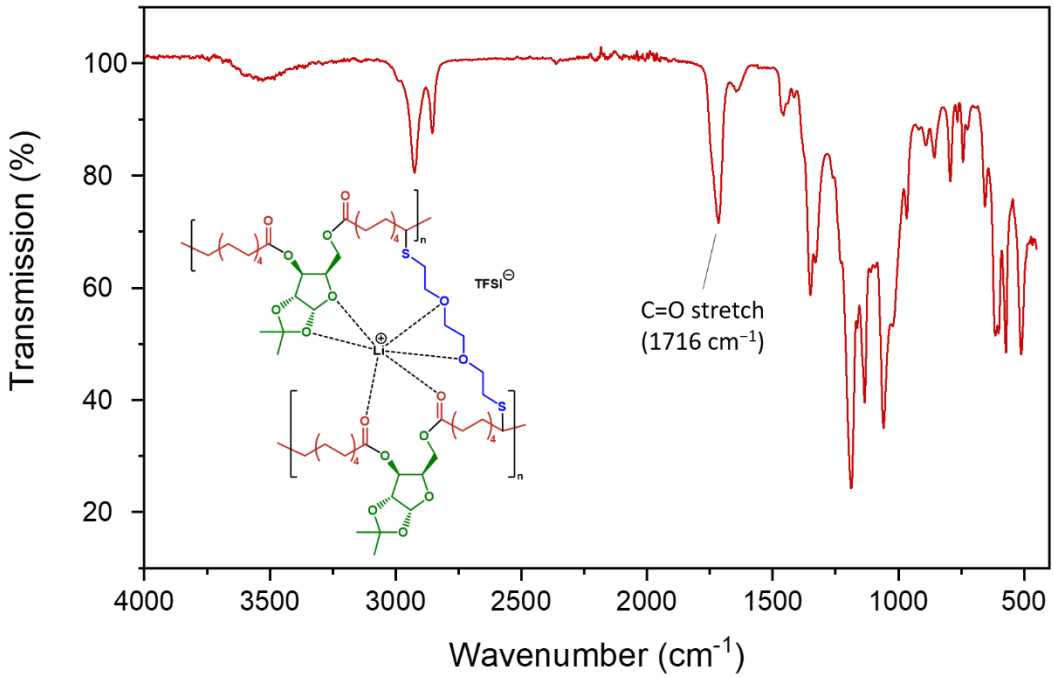


Fig. S4: FTIR spectrum of **1b-100** as a representative SPE. Inset structure shows some of the possible Li^+-ion coordinating sites in the crosslinked polymer.

4. Size-exclusion chromatography (SEC)

All M_n values refer to poly(**1**) or poly(**1**-depr33) prior to crosslinking.

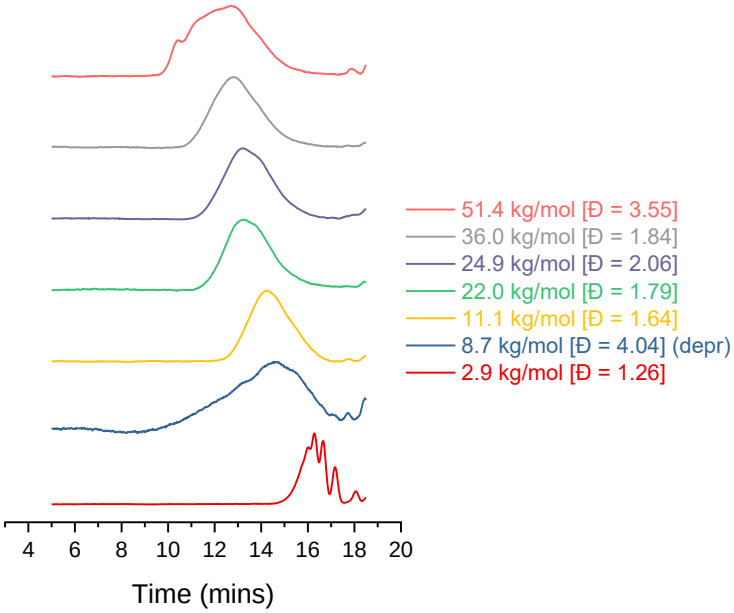


Fig. S5: Stacked SEC traces of selected samples of poly(**1**) and poly(**1**-depr) from Table 1. Samples were prepared THF (1-2 mg mL^{-1}) which was also used as the mobile phase for separation through the column. Detection was achieved using a refractive index method and the system calibrated with polystyrene standards. The blue trace represents the chromatogram for poly(**1**-depr) for which 33% of the protecting ketal groups have been removed to reveal OH groups on the xylose core.

5. Electrochemical impedance spectroscopy (EIS)

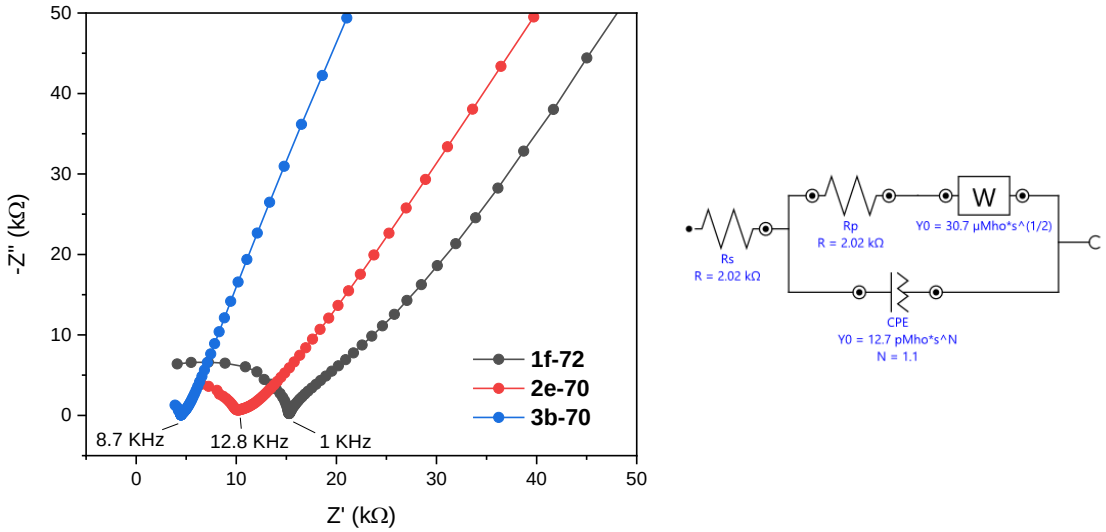


Fig. S6: Nyquist plots of representative SPEs based on poly(**1**-EDDET) measured in the frequency range of 0.1 Hz – 0.5 MHz. An example Randles circuit fitting for **3b-70** is shown on the right where R_p is equivalent to the bulk resistance R_b. For reference, the frequency corresponding to R_b is shown at the intersection of the semi-circle and straight line due to Warburg diffusion on the Nyquist plot.

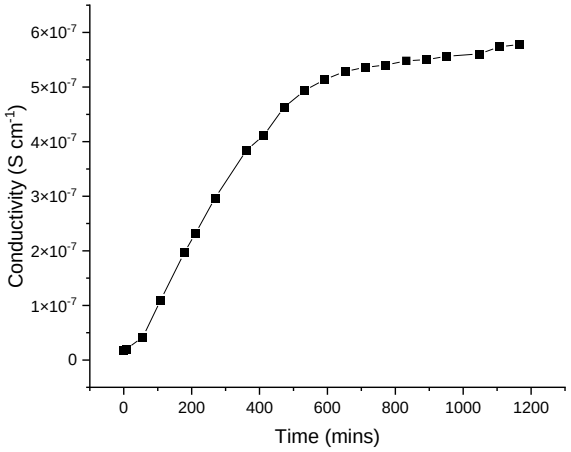


Fig. S7: Chart showing the conductivity hysteresis of SPE **1f-100** ($M_{n,SEC}$ = 2.9 kg mol^{-1}, salt molarity = 100 mol%, 1.0 EDDET equivalents) measured over 12 hours at 68 °C.

6. Conductivity normalisation

Table S1: Example of raw data used for the temperature normalisation to 60 °C for **1a-72**.

T	T	1000/T	R_b	σ	log(σ)
(°C)	(K)	(K^{-1})	(Ω)	(S cm^{-1})	(S cm^{-1})
27	300	3.33	7.64×10^{-5}	1.5×10^{-7}	−6.8
33	306	3.27	3.08×10^{-5}	3.8×10^{-7}	−6.4
40	313	3.19	1.41×10^{-5}	8.4×10^{-7}	−6.1
52	325	3.08	3.68×10^{-4}	3.2×10^{-6}	−5.5
62	335	2.99	1.31×10^{-4}	9.0×10^{-6}	−5.0

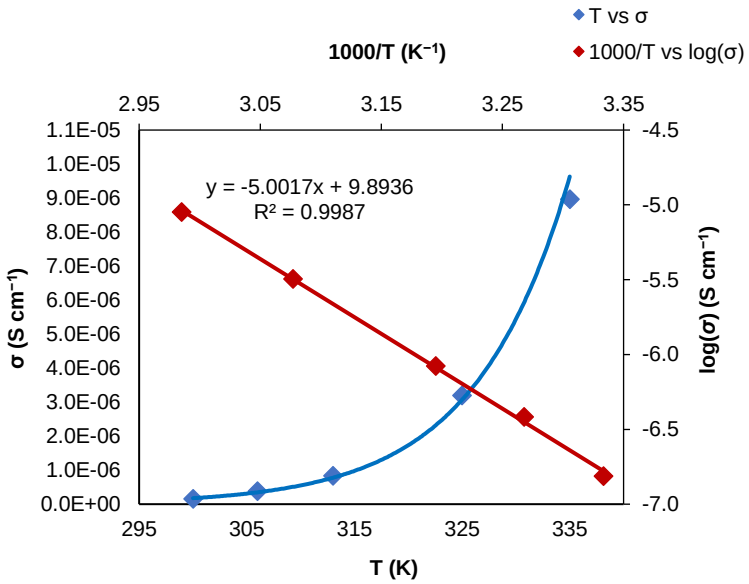


Fig. S8: Plot of raw conductivity data and Arrhenius plot of **1a-72** used for temperature normalisation to 60 °C.

The following derivation of a linear equation was used to normalise the conductivity of each sample to 60 °C:

$$\sigma = 10^{(\mathrm{m} \times (1000/T) + \mathrm{c})} \qquad \textbf{(Equation 3)}$$

where m and c are equal to the gradient and y-intercept of the straight line in Fig. S8, and *T* is equal to 333 K.

Table S2: Normalisation of conductivity to 60 °C for **1a-72** using the plotted data in Fig. S8.

Slope (S cm^{-1} K^{-1})	−5.0017
x-intercept (K)	9.8936
Normalisation temperature (K)	333
σ at 60 °C (S cm^{-1})	7.5×10^{-6}

7. Lithium transference number (t_+)

Table S3: Data used for the determination of t_+ for **2e-70** (Fig. 4B).

Repeat	I_0 (A)	I_{SS} (A)	$R_{b,0}$ (Ω)	$R_{b,SS}$ (Ω)	t_+
1	5.188×10^{-8}	4.348×10^{-8}	57820	61782	0.80
2	4.810×10^{-8}	4.152×10^{-8}	57183	61994	0.84
3	4.553×10^{-8}	4.043×10^{-8}	58383	61536	0.87
4	4.224×10^{-8}	3.580×10^{-8}	59118	74330	0.87
5	3.760×10^{-8}	3.062×10^{-8}	61459	83553	0.84
					0.84 (±0.01)

t_+ was calculated using the Bruce-Vincent equation: $$t_+ = \frac{I_{SS}(\Delta V - I_0 R_{b,0})}{I_0(\Delta V - I_{SS} R_{b,SS})}$$

where:

I_0 = current prior to DC polarisation

I_{SS} = steady-state current

$R_{b,0}$ = bulk resistance determined from an EIS measurement prior to DC polarisation

$R_{b,SS}$ = bulk resistance determined from an EIS measurement after steady-state current is reached

ΔV = polarisation potential (= 0.01 V)

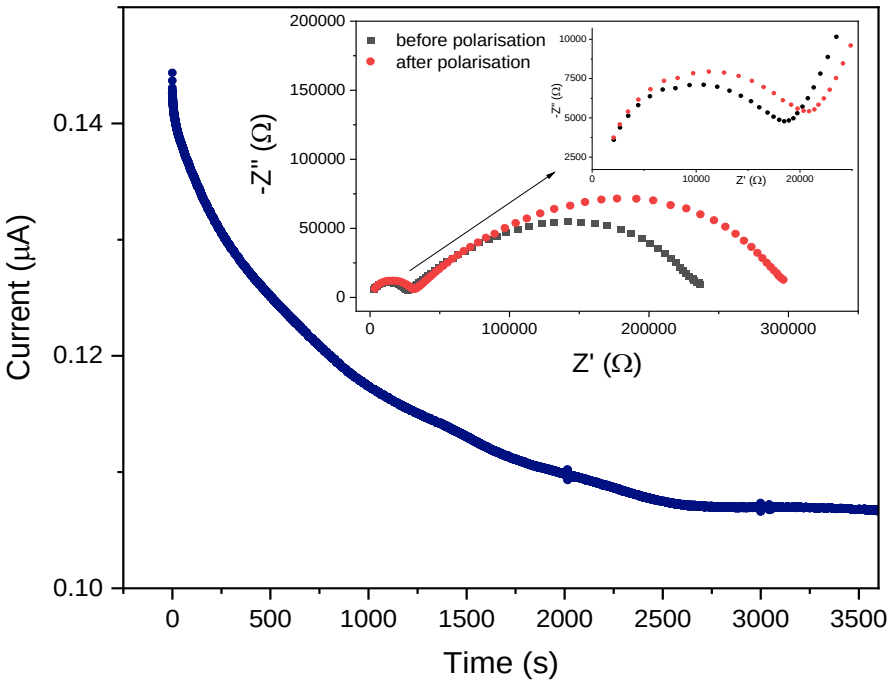


Fig. S9: Additional chronoamperometry and Nyquist plot (inlayed) obtained for a representative SPE sample (M_n 12.4 kg/mol, 70 mol% LiTFSI, 0.05 equivs EDDET, T_g = 9 °C). A 10 mV polarization voltage was applied for 1 hour in a symmetrical Li|SPE|Li cell. The Nyquist plot was obtained by EIS recorded in the frequency range of 0.1 Hz – 1 MHz before and after the chronoamperometry experiment. A t_+ value of 0.66 was determined using the Bruce-Vincent equation.

8. Oligomeric SPE study

Table S4: Conductivity data for SPE films based on an oligomeric sample of poly(**1**).

Entry	SPE reference	$M_{n,SEC}$[a] (kg mol^{-1})	Crosslinker equivalents[d]	Salt mol%[b] [wt%][c]	T_g[e] (°C)	Conductivity[f] (S cm^{-1})
1	**1f-0**	2.9	1.0	0 [0]	−23	—
2	**1f-25**	2.9	1.0	25 [15]	−23	5.3×10^{-7}
3	**1f-40**	2.9	1.0	40 [23]	−7	5.8×10^{-6}
4	**1f-50**	2.9	1.0	50 [29]	−10	1.6×10^{-6}
5	**1f-60**	2.9	1.0	60 [35]	−7	4.7×10^{-6}
6	**1f-72**	2.9	1.0	72 [42]	−25	7.5×10^{-6}
7	**1f-85**	2.9	1.0	85 [49]	−15	1.7×10^{-6}
8	**1f-100**	2.9	1.0	100 [58]	4	9.8×10^{-7}

[a] Refers to molar mass of poly(**1**) prior to crosslinking. [b] Salt mol% calculated as a percentage of moles of salt relative to total number of polymer repeat units moles present. [c] Salt wt% is in reference to the polymer mass prior to crosslinking. [d] Calculated as ratio of EDDET mols to total number of polymer repeat units moles present. [e] Obtained from the second cooling and heating cycle on the DSC thermogram. [f] Normalised to 60 °C using linear regression of an Arrhenius plot of 1000/T vs log(σ).

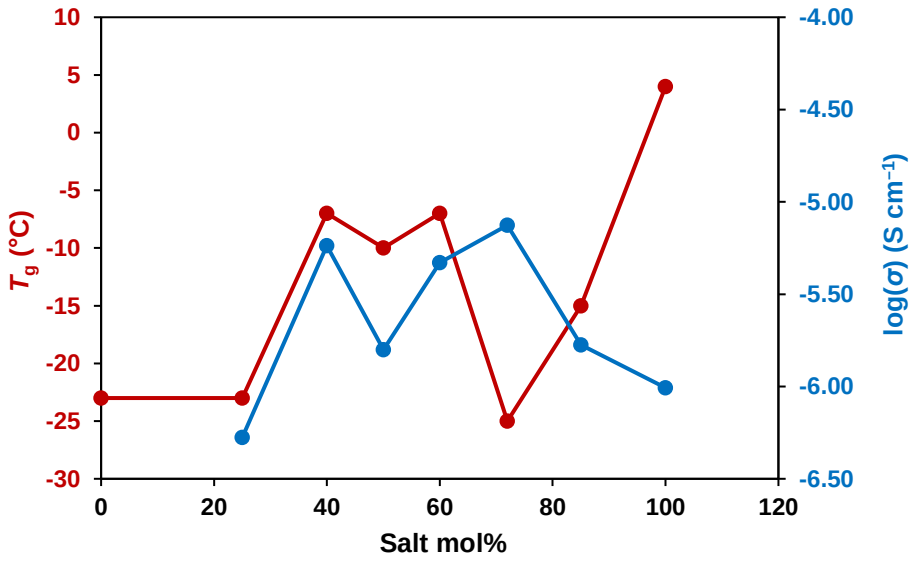


Fig. S10: Chart of T_g and conductivity *vs* salt molarity for oligomeric samples of poly(**1**) crosslinked with 1.0 EDDET equivalents.

9. Differential scanning calorimetry (DSC)

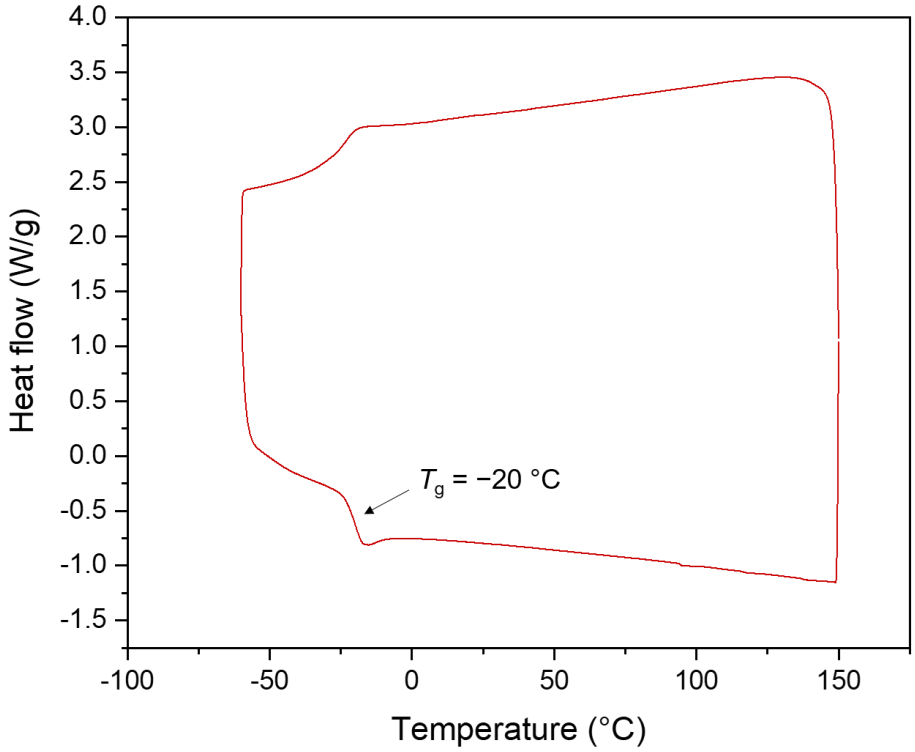


Fig. S11: Representative DSC thermogram showing the second cooling and heating cycle of a sample of poly(**1**) (Table 1, entry 5; $M_{n,SEC}$ = 24.7 kg mol^{-1}). T_g = −20 °C.

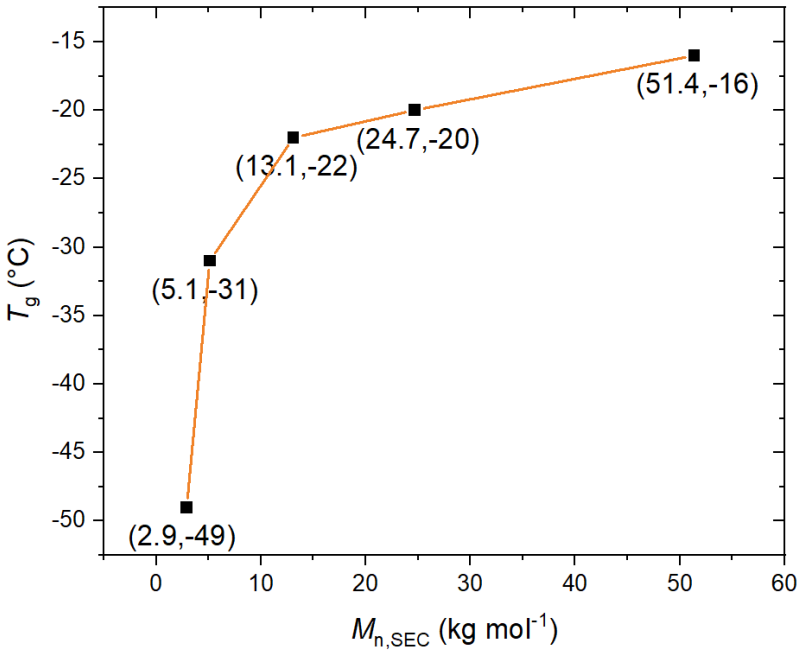


Fig. S12: Plot of molecular weight vs T_g obtained from the second heating cycle in the DSC thermogram for samples of poly(**1**).

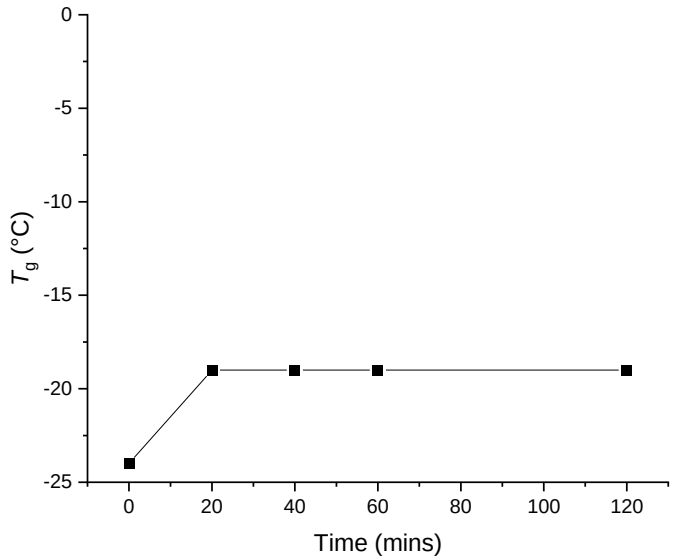


Fig. S13: Chart showing the rate of crosslinking as determined by the increase in T_g of poly(**1**). $M_{n,SEC}$ = 24.7 kg mol^{-1}, salt molarity = 0 mol%, crosslinker equivalents = 0.05.

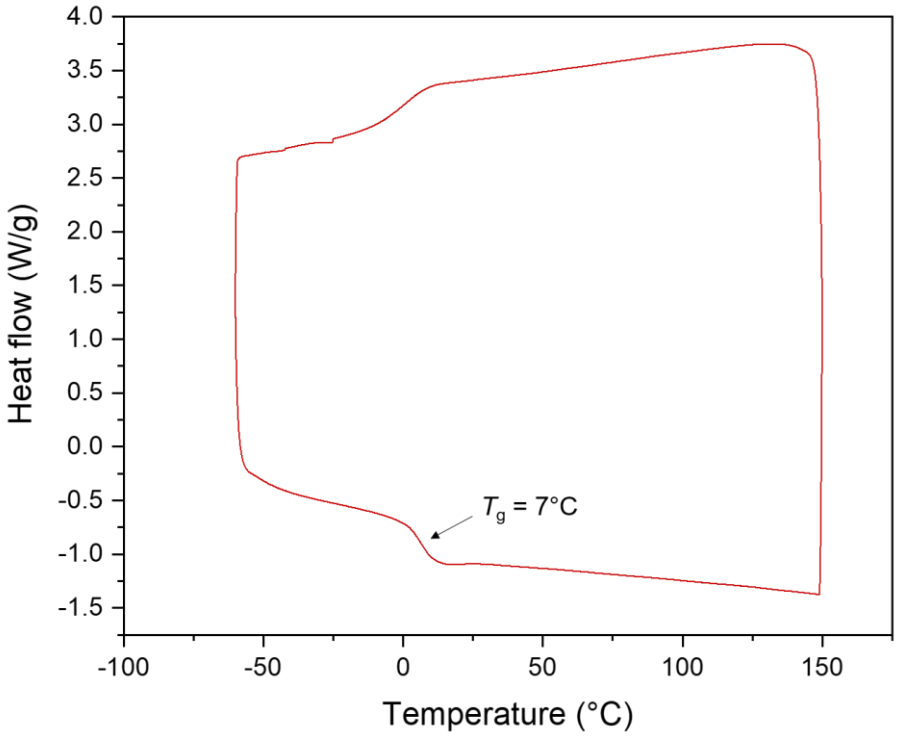


Fig. S14: Representative DSC thermogram of an SPE (**3b-70)** showing the second cooling and heating cycle (Table 2, entry 9; $\boldsymbol{M_{n,SEC}}$ = 24.9 kg mol^{-1}, crosslinker equivalents = 0.05, salt amount = 70 mol%). $\boldsymbol{T_g}$ = 7 °C.

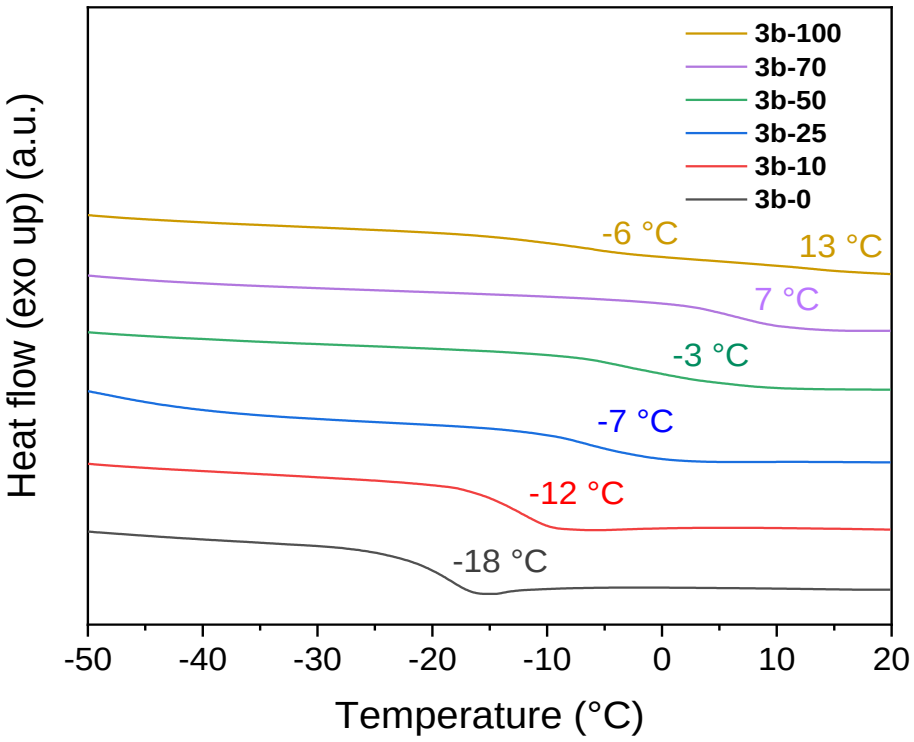


Fig. S15: Plot showing the second heating cycle traces obtained from the DSC thermograms of SPEs **3b-x** with varying amounts of LiTFSI (traces are y-offset and zoomed into *T*g region for clarity).

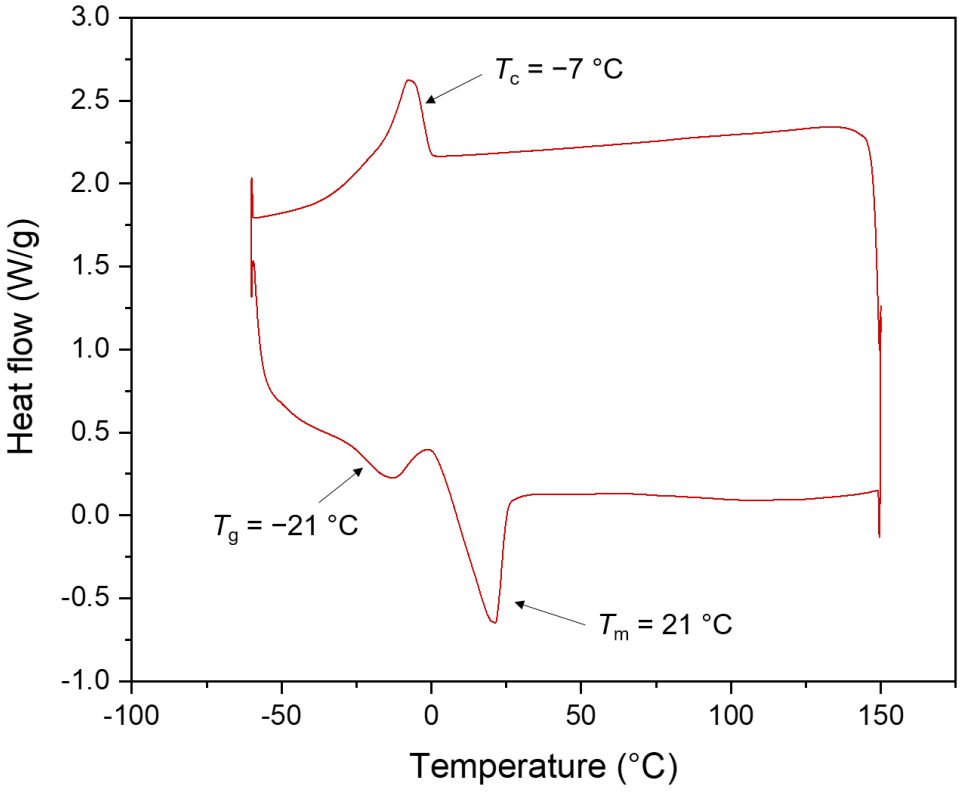


Fig. S16: Second cooling and heating cycle in the DSC thermogram of poly(**1**-depr33). $\boldsymbol{T_g}$ = −21 °C, $\boldsymbol{T_m}$ = 21 °C.

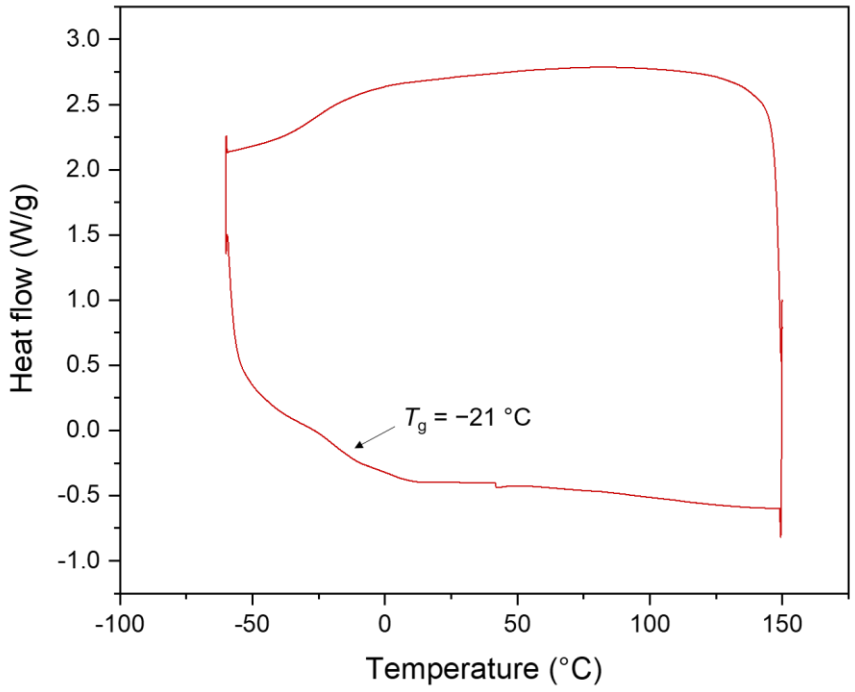


Fig. S17: Second cooling and heating cycle in the DSC thermogram of **5b(depr)-70**. T_g = −21 °C.

10. Uniaxial tensile strength testing

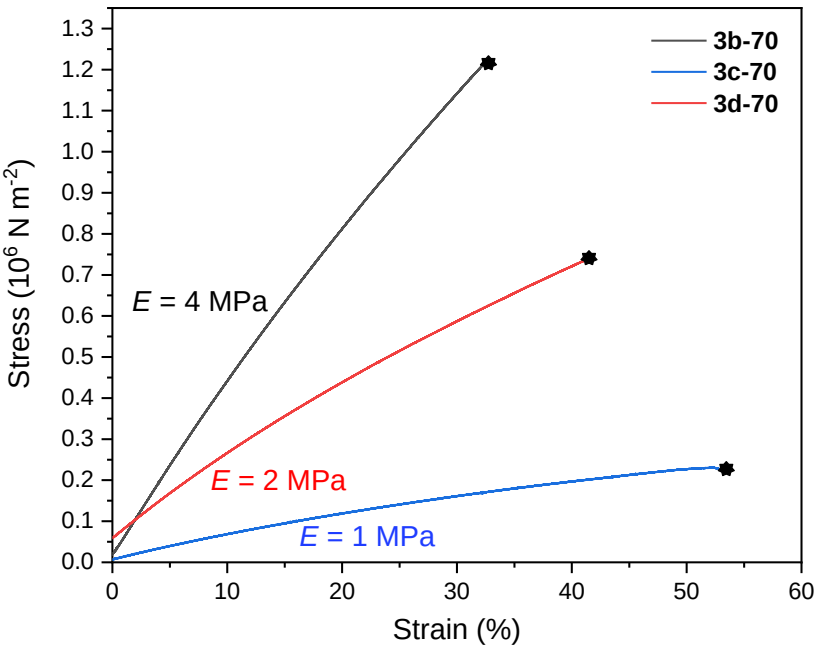
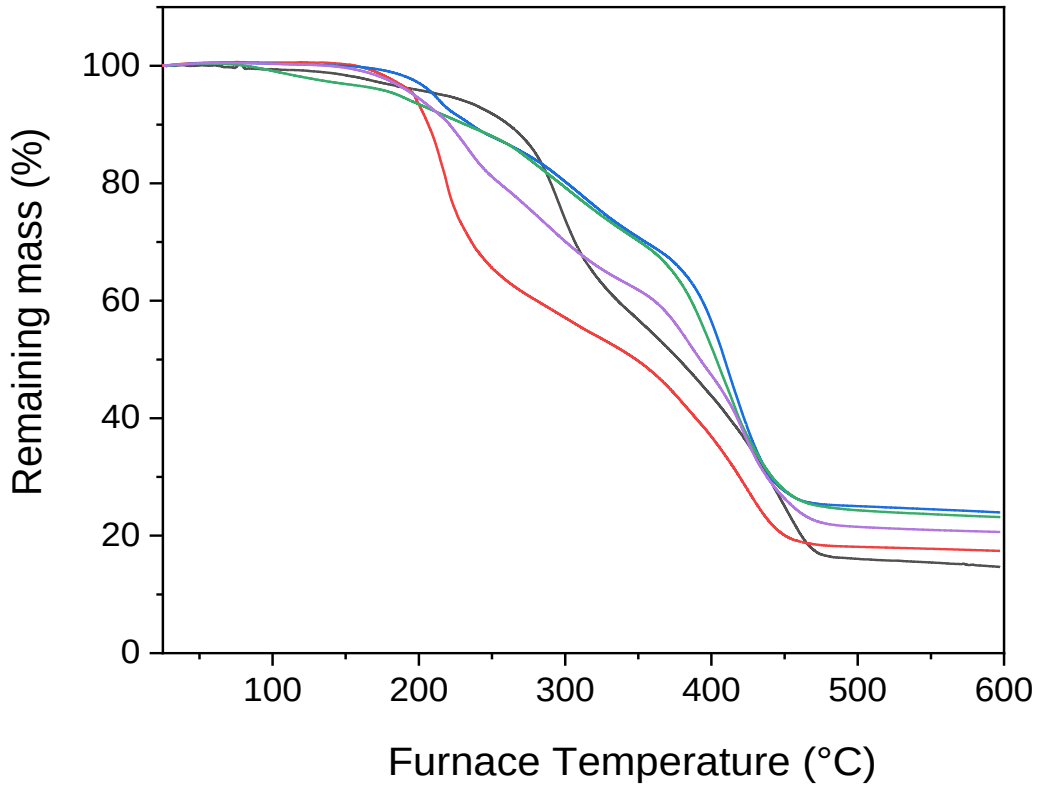


Fig. S18: Stress-strain plot demonstrating the uniaxial strength performance of three SPE's with a crosshead speed of 1 mm min^{-1}. The black spots represent the break point. E = Young's modulus.

Fig. S19: Photograph of the uniaxial tensile strength apparatus setup. Samples were cut into dimensions of approximately 4 mm × 20 mm and clamped between 50 N pneumatic grips. The exposed sample had a starting length of 20 mm.

11. Thermogravimetric analysis (TGA)



	T_{d1} (°C)	T_{d2} (°C)
poly(**1**-EDDET)	297	451
1f-72	219	424
2e-70	234	423
3b-70	213	410
5b-(depr)70	295	416

Fig. S20: TGA trace poly(**1**) ($M_{n,SEC}$ = 13.1 kg mol^{-1}) crosslinked with 10 equivalents of EDDET (black) and representative SPE samples (T_{d1} and T_{d2} refer to temperatures for the maximum of the derivative peaks).