Supplementary Information for:

Poly(vinyl ester 1,2,3-triazolium)s: a New Addition to the Poly(Ionic Liquid)s Family

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Materials. Diisopropylethylamine (DIPEA, 99%), 1-pentyne (**2**, 99%) copper(I) iodide triethylphosphite ($CuIP(OEt)_3$, 97%), vinyl acetate (**4**, 99%), palladium(II) acetate ($Pd(OAc)_2$, 98%), 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO, 98%), lithium bis(trifluoromethane)sulfonimide (LiTFSI, >99%) and *N*-methyl bis[(trifluoromethyl)sulfonyl]imide (**7**, >90%), were purchased from Aldrich and used as received. Dimethylsulfoxide (DMSO) used for polymerization experiments was dried over molecular sieves and degassed by bubbling argon for 15 min. 4-Azidovaleric acid **1**,[1] and alkyl-cobalt(III) ($[Co(acac)_2\text{-}(CH(OCOCH_3)CH_2)_{<4}\text{-}R_0)]$),[2] were synthesized as described earlier.

Characterization methods

NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C. Spectra were obtained with a 5-mm QNP probe at 363 K. Chemical shifts (δ) are given in ppm in reference to residual hydrogenated solvents.

Size exclusion chromatography (SEC) characterization of poly(vinyl ester 1,2,3-triazole) $\mathbf{6_{a\text{-}d}}$ were performed in tetrahydrofuran (THF) at 45 °C with a flow rate of 0.7 mL/min. Polymers were eluted with a Viscotek TDA 305 triple detection (refractometer, viscosimeter and low angle laser light scattering) setup equipped with styragel HR columns (four columns HP PL gel 5 μm, 10^5 Å, 10^4 Å, 10^3 Å and 10^2 Å; separation range from 400 to 4×10^6 g/mol). Number average molar masses (M_n), weight average molar masses (M_w) and chain dispersities ($Đ = M_w/M_n$) were calculated using a calibration curve obtained from polystyrene standards.

SEC characterization of poly(vinyl ester 1,2,3-triazolium) **8** were performed in THF containing 10 mM LiTFSI (flow rate: 1 mL/min) at 35 °C using a SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer index detector 2000 according to a previously reported procedure.[3] PSS SDV analytical linear S 5μm column (molar mass range: 100-150000 Da) and protected by a PL gel 5μm guard column, was calibrated with PS standard (580 g/mol – 467000 g/mol).

Differential scanning calorimetry (DSC) experiments were performed on a DSC Q200 (TA Instruments) at a heating rate of 10 °C/min and a helium flow of 25 mL/min. T_g values were measured during the second heating cycle. Thermogravimetric analysis (TGA) experiments were performed on a TGA Q500 apparatus (TA Instruments) at a heating rate of 10 °C/min and a helium flow of 60 mL/min. Ionic conductivities measurements were repeated three times using a high resolution Alpha-Analyzer (Novocontrol GmbH) assisted by a Quatro temperature controller. Poly(vinyl ester 1,2,3-triazolium) **8** was solvent casted from acetone onto a platinum electrode and annealed at 110 °C under vacuum for ca. 24 h in order to eliminate solvent residuals and adsorbed water. The second platinum electrode was then placed on top of the polymer films using a 50 μm thick Teflon spacer to build-up a measurement cell in a parallel plate configuration with a well-defined distance between electrodes. A further annealing under nitrogen during 4 h at 110 °C was performed in the cryostat of the dielectric spectrometer while monitoring the complex conductivity function $\sigma^*(\omega,T) = \sigma'(\omega,T) + i\sigma''(\omega,T)$. Ionic conductivity measurements were started once a constant value of the complex conductivity function was attained thus affording well equilibrated samples and ensuring the reliability and reproducibility of the measurements. Frequency sweeps were then performed isothermally from 10 MHz to 0.1 Hz by applying a sinusoidal voltage of 0.1 V over temperatures ranging from 110 °C to -70 °C in steps of 10 °C. The temperature was controlled by heating the sample under a flow of pure nitrogen, which excludes the presence of oxygen and humidity in the measurement chamber. The thermal stability was set to be better than 0.1 K in absolute values with relative variations less than 0.2 K/min.

Synthesis of 1,2,3-triazole-functionalized carboxylic acid 3

$CuIP(OEt)_3$ (3.47 g, 9.70 mmol) and DIPEA (12.5 g, 97.0 mmol) were added to a solution of 4-azidovaleric acid **1** (13.9 g, 97.2 mmol) and 1-pentyne **2** (7.27 g, 107 mmol) in tetrahydrofuran (100 mL). The mixture was stirred under argon for 24 h at 45 °C before being evaporated to dryness under reduced pressure. The crude crude product was purified by column chromatography using a 3:7 mixture of petroleum ether and ethyl acetate to yield after evaporation of the solvents under reduced pressure **3** as a white solid (18.5 g, 90.6%). ^1H NMR (DMSO-d_6) δ (ppm): 12.02 (bs, $COO\mathbf{H}$, 1H), 7.82 (s, $C\mathbf{H}{=}CN$, 1H), 4.29 (t, $NC\mathbf{H}_2CH_2CH_2CH_2COOH$, J = 7.0 Hz, 2H), 2.57 (t, $CH{=}CC\mathbf{H}_2CH_2CH_3$, J = 7.6 Hz, 2H), 2.24 (t, $NCH_2CH_2CH_2C\mathbf{H}_2COOH$, J = 7.4 Hz, 2H), 1.84-1.77 (m, $NCH_2C\mathbf{H}_2CH_2CH_2COOH$, 2H), 1.64-1.53 (m, $CH{=}CCH_2C\mathbf{H}_2CH_3$, 2H), 1.48-1.40 (m, $NCH_2CH_2C\mathbf{H}_2CH_2COOH$, 2H), 0.89 (t, $CH{=}CCH_2CH_2C\mathbf{H}_3$, J = 7.2 Hz, 3H). ^{13}C NMR (DMSO-d_6) δ (ppm): 173.9 ($\mathbf{C}OOH$), 146.6 ($CH{=}\mathbf{C}N$), 121.6 ($\mathbf{C}H{=}CN$), 48.7 ($N\mathbf{C}H_2CH_2CH_2CH_2COOH$), 32.9 ($NCH_2CH_2CH_2\mathbf{C}H_2COOH$), 29.1 ($NCH_2\mathbf{C}H_2CH_2CH_2COOH$), 27.0 ($CH{=}C\mathbf{C}H_2CH_2CH_3$), 22.1 ($CH{=}CCH_2\mathbf{C}H_2CH_3$), 21.4 ($NCH_2CH_2\mathbf{C}H_2CH_2COOH$), 13.5 ($CH{=}CCH_2CH_2\mathbf{C}H_3$). HRMS: (ESI, m/z): $[M + H]^+$ calcd for $C_{10}H_{18}N_3O_2$, 212.1394; found, 212.1387.

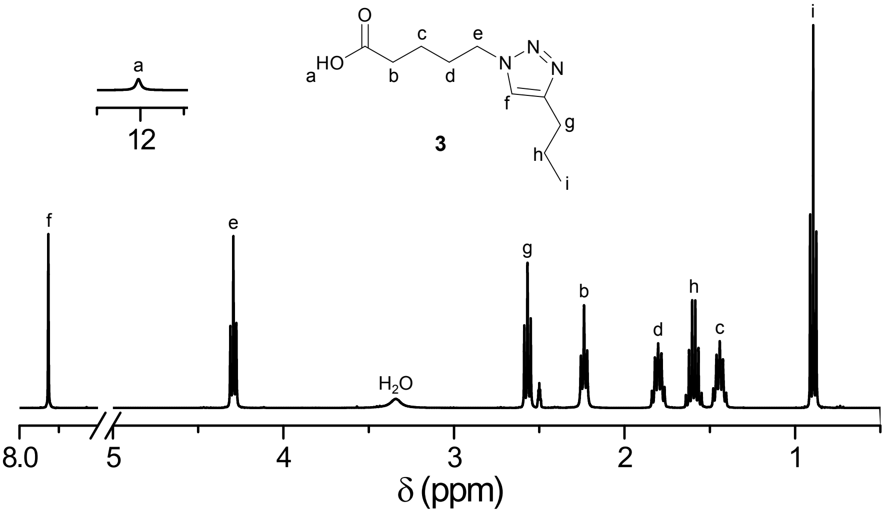

Figure S1. ^1H NMR (DMSO-d_6, 400 MHz) of 1,2,3-triazole-functionalized carboxylic acid **3**.

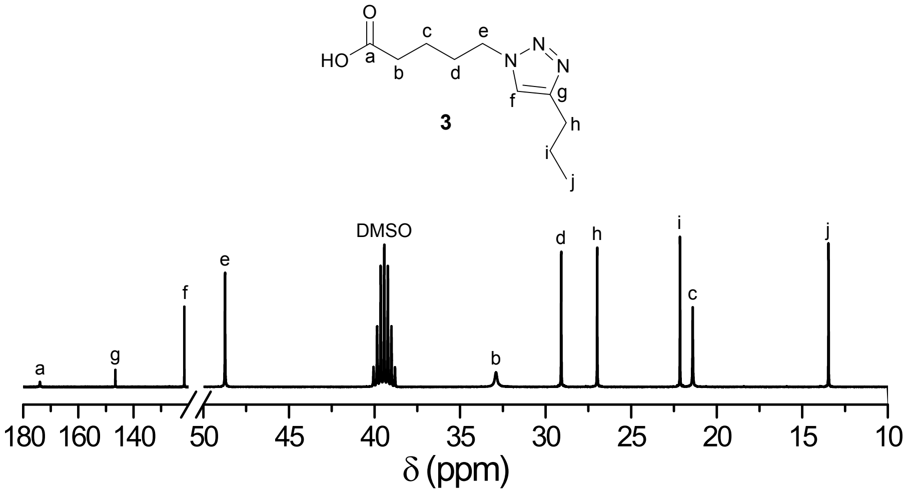

Figure S2. ^{13}C NMR (DMSO-d_6, 100 MHz) of 1,2,3-triazole-functionalized carboxylic acid **3**.

Synthesis of 1,2,3-triazole-functionalized vinyl ester monomer 5

A solution of **3** (8.12 g, 38.5 mmol) and $\mathrm{Pd(OAc)_2}$ (431 mg, 1.92 mmol) in vinyl acetate **4** (33.1 g, 385 mmol) was stirred at 60 °C for 16 h. The solution was then filtered over celite and thoroughly washed with petroleum ether. The crude product was purified by column chromatography using a 3:2 mixture of petroleum ether and ethyl acetate to yield after evaporation of the solvents under reduced pressure **5** as a slightly yellow viscous liquid (6.19 g, 68.7%). ^{1}H NMR (DMSO-d_6) δ (ppm): 7.84 (s, $\mathrm{C\mathbf{H}{=}CN}$, 1H), 7.21 (dd, J_1 = 6.4 Hz, J_2 = 14 Hz, $\mathrm{C\mathbf{H}{=}CH_2}$, 1H), 4.87 (dd, J_1 = 1.6 Hz, J_2 = 14 Hz, $\mathrm{CH{=}CH\mathbf{H}}$, 1H), 4.64 (dd, J_1 = 1.6 Hz, J_2 = 6.4 Hz, $\mathrm{CH{=}C\mathbf{H}H}$, 1H), 4.31 (t, $\mathrm{NC\mathbf{H}_2CH_2CH_2CH_2COOCH{=}CH_2}$, J = 7.0 Hz, 2H), 2.57 (t, $\mathrm{CH{=}CC\mathbf{H}_2CH_2CH_3}$, J = 7.6 Hz, 2H), 2.46 (t, $\mathrm{NCH_2CH_2CH_2C\mathbf{H}_2COOCH{=}CH_2}$, J = 7.4 Hz, 2H), 1.86-1.78 (m, $\mathrm{NCH_2C\mathbf{H}_2CH_2CH_2COOCH{=}CH_2}$, 2H), 1.65-1.54 (m, $\mathrm{CH{=}CCH_2C\mathbf{H}_2CH_3}$, 2H), 1.54-1.44 (m, $\mathrm{NCH_2CH_2C\mathbf{H}_2CH_2COOCH{=}CH_2}$, 2H), 0.89 (t, $\mathrm{CH{=}CCH_2CH_2C\mathbf{H}_3}$, J = 7.2 Hz, 3H). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm) δ: 170.1 ($\mathrm{\mathbf{C}OOCH{=}CH_2}$), 146.6 ($\mathrm{CH{=}\mathbf{C}N}$), 141.1 ($\mathrm{\mathbf{C}H{=}CH_2}$), 121.6 ($\mathrm{\mathbf{C}H{=}CN}$), 98.0 ($\mathrm{CH{=}\mathbf{C}H_2}$), 48.6 ($\mathrm{N\mathbf{C}H_2CH_2CH_2CH_2COOCH{=}CH_2}$), 32.2 ($\mathrm{NCH_2CH_2CH_2\mathbf{C}H_2COOCH{=}CH_2}$), 28.9 ($\mathrm{NCH_2\mathbf{C}H_2CH_2CH_2COOCH{=}CH_2}$), 27.0 ($\mathrm{CH{=}C\mathbf{C}H_2CH_2CH_3}$), 22.2 ($\mathrm{CH{=}CCH_2\mathbf{C}H_2CH_3}$), 20.9 ($\mathrm{NCH_2CH_2\mathbf{C}H_2CH_2COOCH{=}CH_2}$), 13.5 ($\mathrm{CH{=}CCH_2CH_2\mathbf{C}H_3}$). HRMS: (ESI, m/z): $[\mathrm{M + H}]^+$ calcd for $\mathrm{C_{12}H_{20}N_3O_2}$, 238.1550; found, 238.1547.

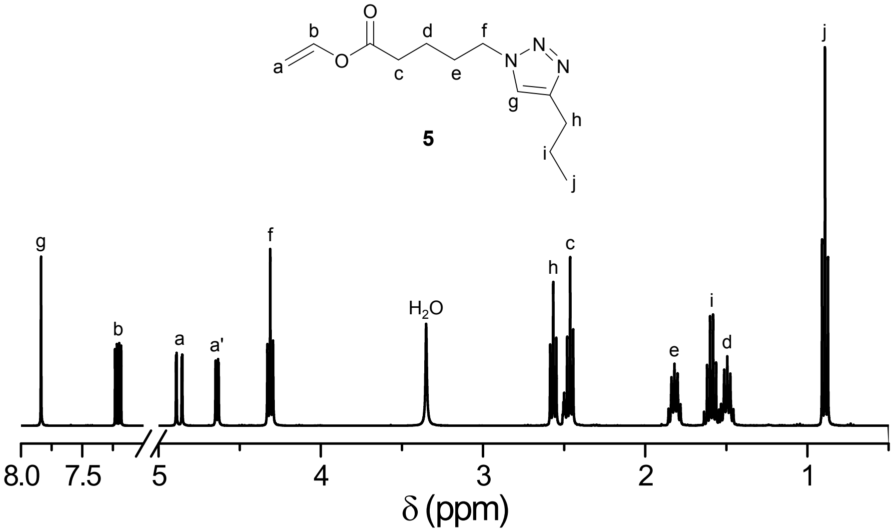

Figure S3. ^{1}H NMR (DMSO-d_6, 400 MHz) of 1,2,3-triazole-functionalized vinyl ester **5**.

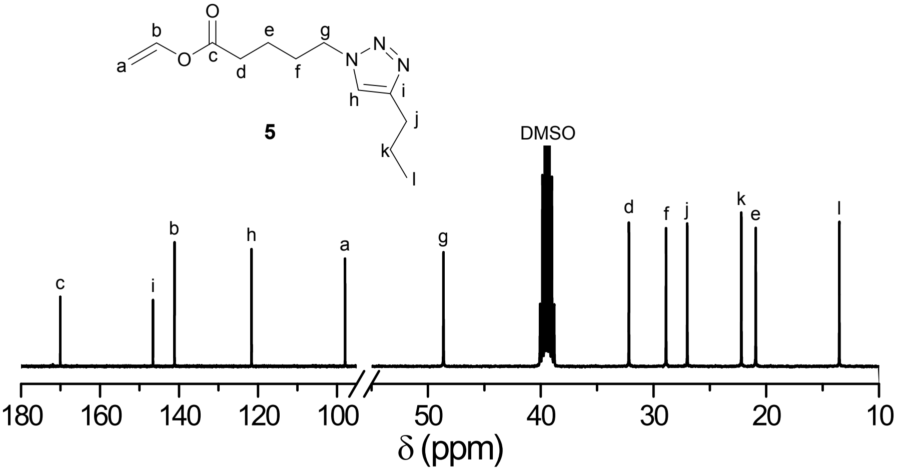

Figure S4. ^{13}C NMR (DMSO-d_6, 100 MHz) of 1,2,3-triazole-functionalized vinyl ester **5**.

Polymerization of 5 by cobalt-mediated radical polymerization, synthesis of 6_d

A solution of alkyl-cobalt(III) (0.34 mL of a 0.248 mol/L stock solution in dichloromethane, 8.4×10^{-5} mol) was introduced in a Schlenk tube and dichloromethane was removed under vacuum at room temperature before adding argon. Degassed and dried DMSO-d_6 (4.0 mL) and **5** (1.0 g, 4.2 mmol) were then added and the solution was stirred at 30 °C under argon. Aliquots were regularly withdrawn to determine monomer conversion by ^{1}H NMR in DMSO-d_6 and to perform SEC in tetrahydrofuran. All samples for SEC analysis were added by excess TEMPO in order to stop the polymerization and to remove the cobalt complex from the polymer chain-ends.[4] After 6.5 hours at 30 °C, the polymerization was terminated by addition of TEMPO, and the crude polymer was dialyzed against water for 24h and freeze-dried. The resulting viscous liquid was dissolved in dichloromethane and precipitated twice in 9:1 mixture of diethyl ether and ethyl acetate maintained at 4 °C to recover $\mathbf{6_d}$ as a colorless viscous solid (conversion = 80%, M_n = 7.2 kDa, $Đ$ = 1.21). Kinetic results are summarized in **Table S1**. ^{1}H NMR (DMSO-d_6, ppm) δ: 7.79 (s, C**H**=CN, 1H), 4.97-4.53 (bs, C**H**CH$_2$O, 1H), 4.26 (bs, NC**H**$_2$CH$_2$CH$_2$CH$_2$COO, 2H), 2.52 (bs, CH=CC**H**$_2$CH$_2$CH$_3$, 2H), 2.36-2.06 (bs, NCH$_2$CH$_2$CH$_2$C**H**$_2$COO, 2H), 2.03-1.49 (bm, CHC**H**$_2$O, 2H), 1.85-1.65 (bm,

$NCH_2C\mathbf{H}_2CH_2CH_2COOH$, 2H), 1.65-1.42 (bm, $CH=CCH_2C\mathbf{H}_2CH_3$, 2H), 1.42-1.29 (bm, $NCH_2CH_2C\mathbf{H}_2CH_2COO$, 2H), 0.85 (bt, $CH=CCH_2CH_2C\mathbf{H}_3$, J = 9.6 Hz, 3H).

Table S1. Kinetic monitoring of the polymerization of **5** mediated by alkyl-cobalt(III).

N°	Time (h)	Monomer conversion (%)	M_{nSEC} (g/mol)[a]	$Đ$
$\mathbf{6_a}$	1.0	38	4700	1.10
$\mathbf{6_b}$	3.0	67	6050	1.19
$\mathbf{6_c}$	6.0	78	6800	1.22
$\mathbf{6_d}$	6.5	80	7200	1.21

Alkylation of $\mathbf{6_d}$ by *N*-methyl bis[(trifluoromethyl)sulfonyl]imide, synthesis of 8

A mixture of poly(vinyl ester 1,2,3-triazole) $\mathbf{6_d}$ (450 mg, 1.90 mmol of 1,2,3-triazole groups) and *N*-methyl bis[(trifluoromethyl)sulfonyl]imide (841 mg, 2.85 mmol) in DMF (2.0 mL) was heated for 24 hours at 110 °C. After evaporation of DMSO under vacuum, the crude compound was dissolved in acetonitrile and precipitated twice in a 4:1 mixture of diethyl ether and ethyl acetate maintained at 4 °C. The turbid solution was centrifuged to recover **8** as a dark brown viscous solid (592 mg, 58.8 %). ^1H NMR (DMSO-d_6, ppm) δ: 8.67 (s, $C\mathbf{H}=CN$, 1H), 4.99-4.53 (bs, $C\mathbf{H}CH_2O$, 1H), 4.52 (bs, $NC\mathbf{H}_2CH_2CH_2CH_2COO$, 2H), 4.16 (bs, $C\mathbf{H}_3N$, 3H), 2.80 (bs, $CH=CC\mathbf{H}_2CH_2CH_3$, 2H), 2.42-2.11 (bs, $NCH_2CH_2CH_2C\mathbf{H}_2COO$, 2H), 2.03-1.49 (bm, $CHC\mathbf{H}_2O$, 2H), 2.02-1.79 (bm, $NCH_2C\mathbf{H}_2CH_2CH_2COOH$, 2H), 1.78-1.58 (bm, $CH=CCH_2C\mathbf{H}_2CH_3$, 2H), 1.58-1.32 (bm, $NCH_2CH_2C\mathbf{H}_2CH_2COO$, 2H), 0.97 (bt, $CH=CCH_2CH_2C\mathbf{H}_3$, J = 9.6 Hz, 3H).

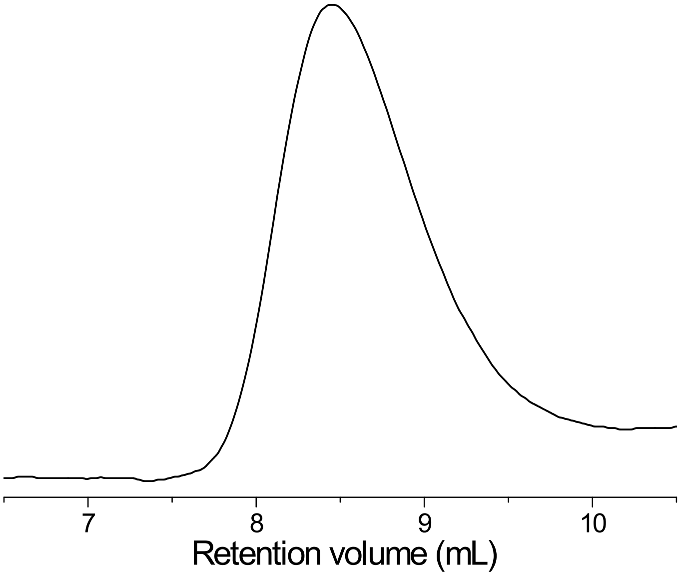

Figure S5. SEC trace (10 mM solution of LiTFSI in THF) of poly(vinyl ester 1,2,3-triazolium) **8**.

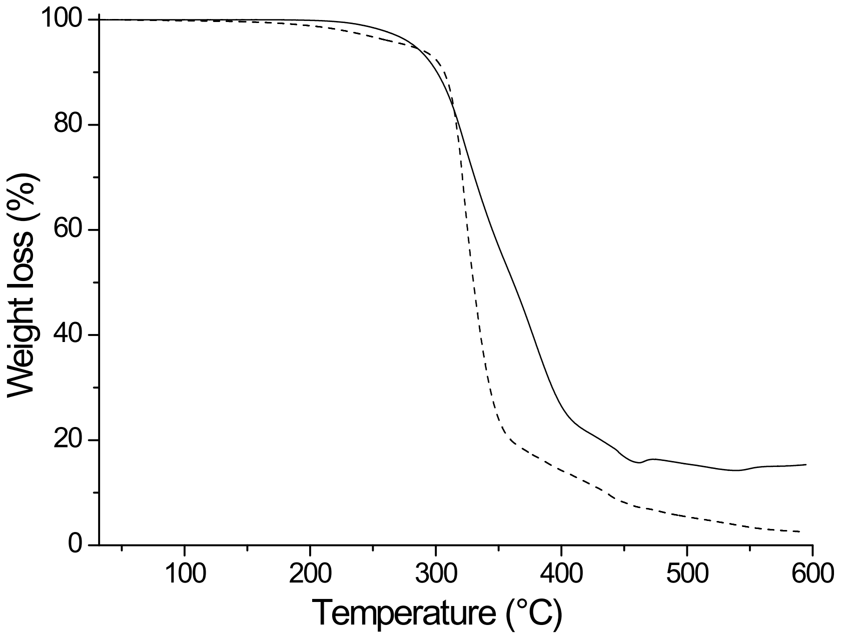

Figure S6. TGA of poly(vinyl ester 1,2,3-triazole) **6_d** (dashed line) and poly(vinyl ester 1,2,3-triazolium) **8** (solid line).

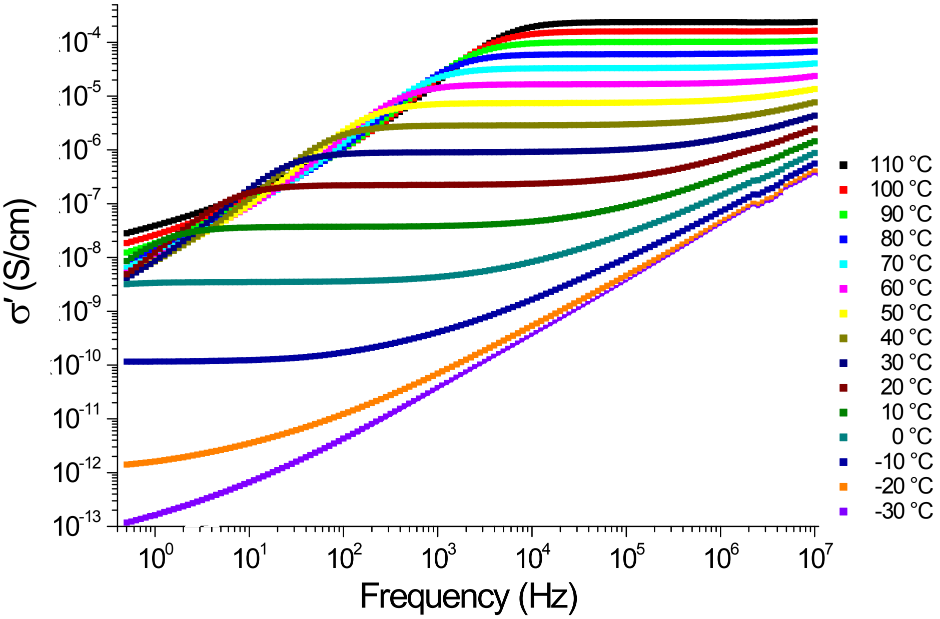

Figure S7. Conductivity versus frequency at different temperatures for poly(vinyl ester 1,2,3-triazolium) **8**.

Table S2. Solubility of poly(vinyl ester 1,2,3-triazole) $\mathbf{6_d}$ and poly(vinyl ester 1,2,3-triazolium) **8**.

Entry	H_2O[a]	Heptane	MeOH	EtOAc	Acetone	Et_2O	THF	CH_2Cl_2	$CHCl_3$	CH_3CN	$PhCH_3$	DMF	DMSO
$\mathbf{6_d}$	-	-	++	+	++	-	++	++	++	++	+	++	++
8	-	-	+	-	++	-	+	-	-	++	-	++	++

[a] "++" indicates solubility at 10 mg/mL, "+" indicates solubility at 1 mg/mL, while "-" indicates no detectable solubility at 1 mg/mL.

References

1) H. Kakwere, R. J. Payne, K. A. Jolliffe and S. Perrier, *Soft Matter* 2011, **7**, 3754.

2) A. Debuigne, Y. Champouret, R. Jerome, R. Poli and C. Detrembleur, *Chem. Eur. J.*, 2008, **14**, 4046.

3) H. He, M. Zhong, B. Adzima, D. Luebke, H. Nulwala and K. Matyjaszewski, *J. Am. Chem. Soc.* 2013, **135**, 4227.

4) A. Debuigne, J.-R. Caille and R. Jerome, *Macromolecules* 2005, **38**, 5452.