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Unprecedented Scissor Effect of Macromolecular Cross-linkers on the Glass Transition Temperature of Poly(*N*-vinylimidazole), Crystallinity Suppression of Poly(tetrahydrofuran) and Molecular Mobility by Solid State NMR in Poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) Conetworks

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Synthesis of methacrylate-telechelic poly(tetrahydrofuran) (PTHFDMA) macromonomers: for the lower molecular weight cross-linker the macromolecular methacrylate-telechelic PTHF (PTHFDMA) were prepared by reacting hydroxyl-ended poly(tetrahydrofuran) (PTHFDOH) with methacryloyl chloride. The synthesis of the higher molecular weight dimetachrylate terminated poly(tetrahydrofuran)s (PTHFDMA) macromonomers have been obtained by cationic ring opening polymerization of tetrahydrofuran (THF) by initiation with trifluoromethanesulfonic anhydride (Tf_2O) and end-capping of the living chains with sodium methacrylate (MANa). Freshly distilled THF (200 mL, 2.48 mol) was added in a 500 mL two-necked flask with a magnetic stirring rod, and it was evacuated and purged with dry nitrogen. Freshly distilled Tf_2O (0.42 mL, 2.48 mmol) was added to dry THF under permanent stirring. A chloroform suspension of MANa (2.6801 g, 24.8 mmol) was added to the reaction mixture after predetermined time (35 min for PTHFDMA macro-cross-linker of M_n 10000 g/mol). After 48 hour reaction time the solvent was evaporated and the polymer was precipitated

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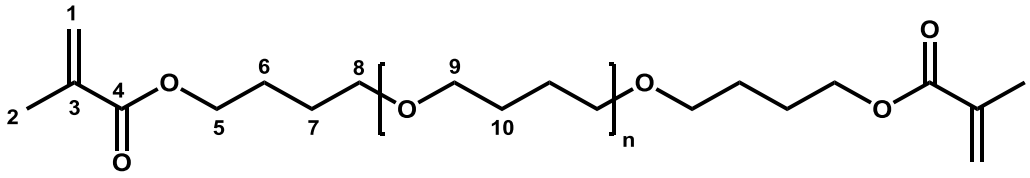
into water/methanol (1/1) solvent under permanent stirring. The product was dissolved in THF and filtration of polymer solutions through columns of aluminum oxide and silica gel have been developed for the removal of contaminations. The solvent was evaporated and the yield of 25.32 g (14.24%) PTHFDMA was obtained. The efficiency of the end-group modification was confirmed by ^{1}H-NMR (functionality = 2.0).



^{1}H NMR ($CDCl_3$): δ [ppm] = 1.62 (4H; $H_{7,10}$; m), 1.76 (4H; H_6; m), 1.94 (2H; H_2; s), 3.41 (4H $H_{8,9}$; m), 4.17 (4H; H_5; t), 5.54 (1H; H_{1trans};m), 6.09 (1H; H_{1cis};m)

Table S1 Characterization of the PTHF dimethacrylate macromonomers (PTHFDMA) obtained by cationic ring opening polymerization.

Sample	M_n[a] (g/mol)	M_n[b] (g/mol)	M_w/M_n[b]	Yield (%)
PTHFDMA7k	6850	8650	1.19	11.6
PTHFDMA10k	10000	11550	1.21	14.2

(a) ^{1}H NMR
(b) GPC

Differential scanning calorimetry (DSC) analyses were carried out in order to reveal the phase behavior of the components and crystallinity of PTHF in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF, "*l*" stands for "*linked by*") conetworks. Original DSC thermograms and enlarged insets of annealed pure PVIm homopolymer, PTHF macromolecular cross-linkers and PVIm-*l*-PTHF conetwork samples are shown in Fig. S1, Fig. S2-S4 and Fig. S5-S22, respectively. The glass transition temperature (T_g) values of the PVIm and PTHF components of the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks as a function of composition, enlarged in both temperature ranges, are shown in Fig. S23 and Fig. S24, respectively. Parameters (Compositions, melting points, crystalline fractions (X_c) and glass transition temperatures (T_g))of the blends consist of poly(*N*-vinylimidazole)

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(PVIm) and poly(tetrahydrofuran) with varying molecular weights are shown in Table S2. Original DSC thermograms and enlarged insets of annealed blends of PTHF and PVIm homopolymers consist PVIm and PTHF with varying composition and molecular weights of poly(tetrahydrofuran), enlarged in both temperature ranges, are shown in Fig. S25- S29, respectively.

Cross polarization magic angle spinning NMR spectra of V7k-52 poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) sample at 45 ^{o}C with contact time of 2ms. The spinning speed was 8 kHz, shown in Fig. S30. Time coefficient of the cross polarization (T_{CH}) of the aromatic and aliphatic carbons of the poly(*N*-vinylimidazole) phase above the melting temperature of poly(tetrahydrofuran) (at 45 ^{o}C) as a function of the average molecular weights of the hydrophilic PVIm segments between two cross-linking points (M_c) in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks, are shown in Fig. S31 and Fig. S32, respectively.

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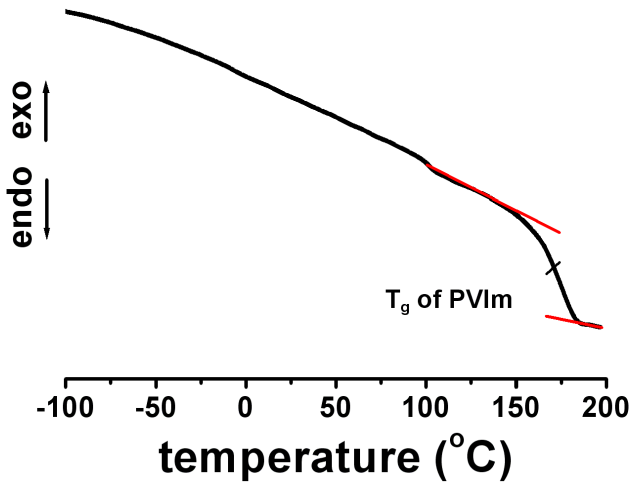

Fig. S1 Differential scanning calorimetry (DSC) thermogram (second heating scan) of PVIm pure homopolymer (heating rate = 10 °C/min).

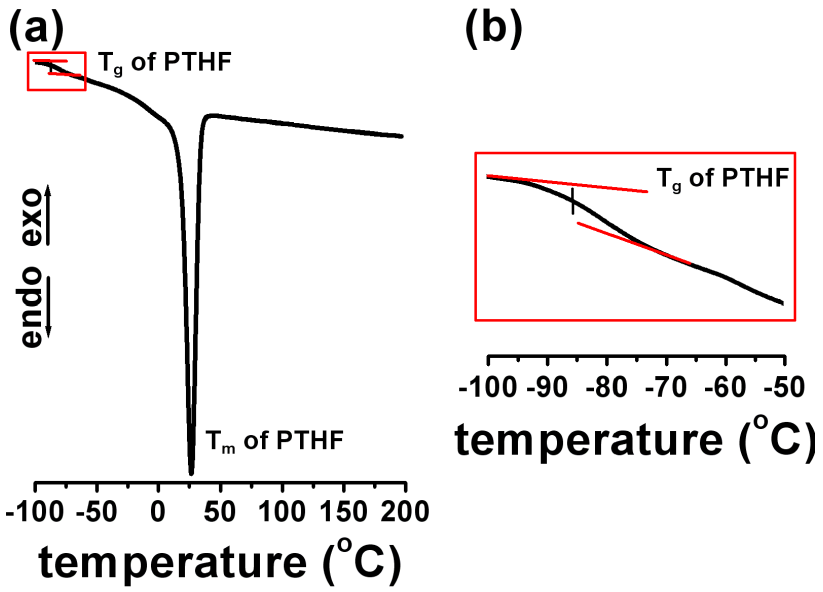

Fig. S2 Differential scanning calorimetry (DSC) thermogram (second heating scan) of PTHFDMA2k (M_n of 2170 g/mol) pure macromolecular cross-linker (a) and enlargement of the thermogram in the -100 to -50 °C temperature range (b) (heating rate = 10 °C/min).

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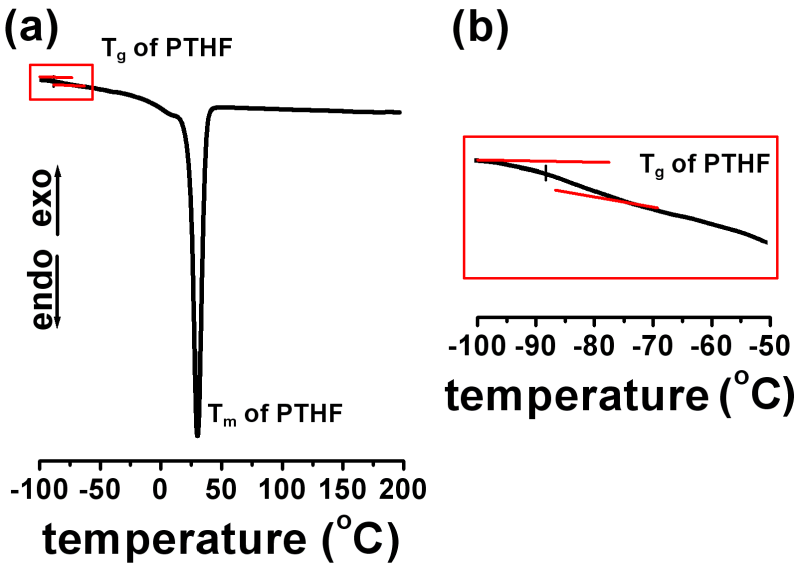

Fig. S3 Differential scanning calorimetry (DSC) thermogram (second heating scan) of PTHFDMA7k (M_n of 6850 g/mol) pure macromolecular cross-linker (a) and enlargement of the thermogram in the -100 to -50 °C temperature range (b) (heating rate = 10 °C/min).

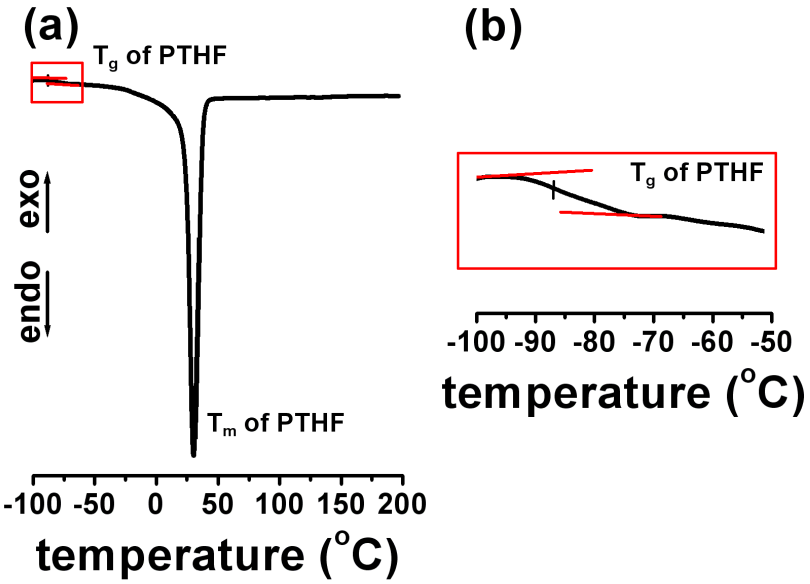

Fig. S4 Differential scanning calorimetry (DSC) thermogram (second heating scan) of PTHFDMA10k (M_n of 10000 g/mol) pure macromolecular cross-linker (a) and enlargement of the thermogram in the -100 to -50 °C temperature range (b) (heating rate = 10 °C/min).

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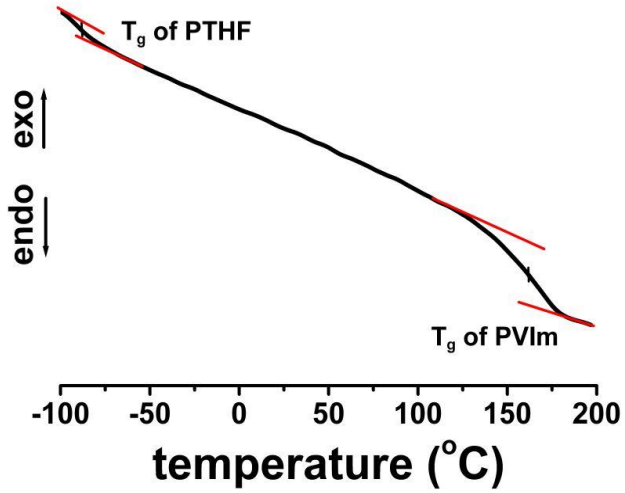

Fig. S5 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V2k-25 (25 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 2170 g/mol (heating rate = 10 °C/min).

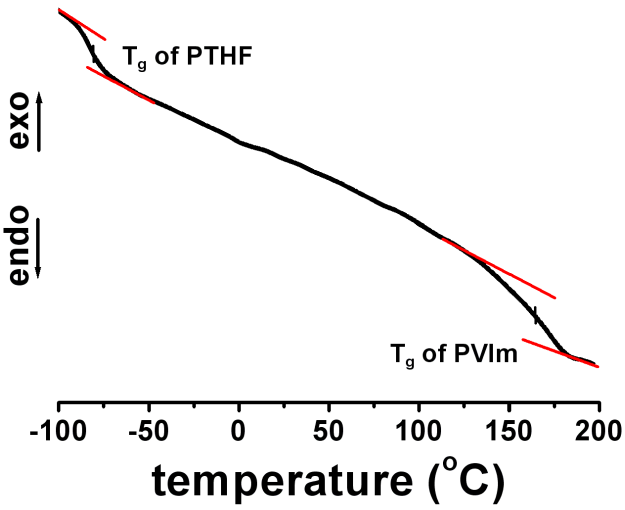

Fig. S6 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V2k-38 (38 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 2170 g/mol (heating rate = 10 °C/min).

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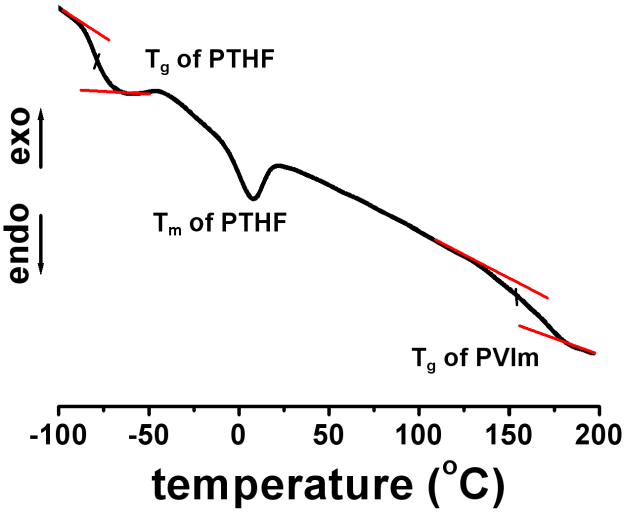

Fig. S7 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V2k-47 (47 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 2170 g/mol (heating rate = 10 °C/min).

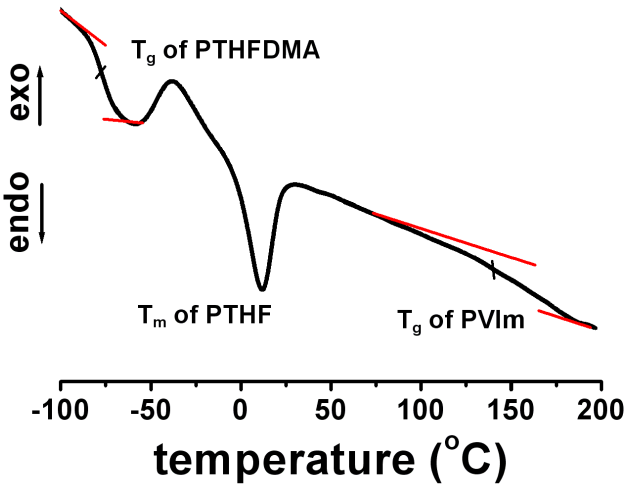

Fig. S8 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V2k-59 (59 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 2170 g/mol (heating rate = 10 °C/min).

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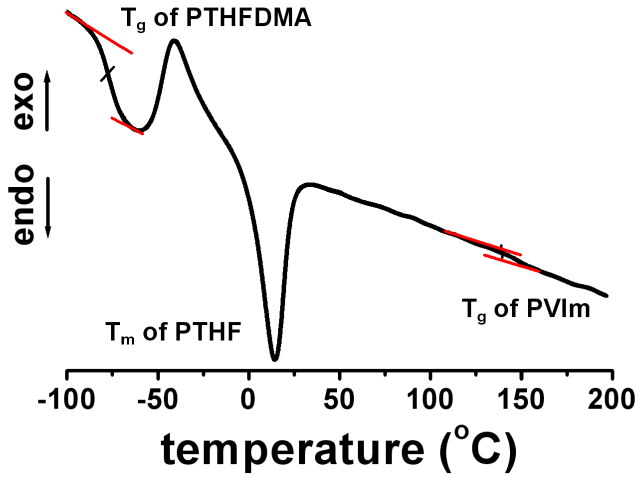

Fig. S9 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V2k-74 (74 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 2170 g/mol (heating rate = 10 °C/min).

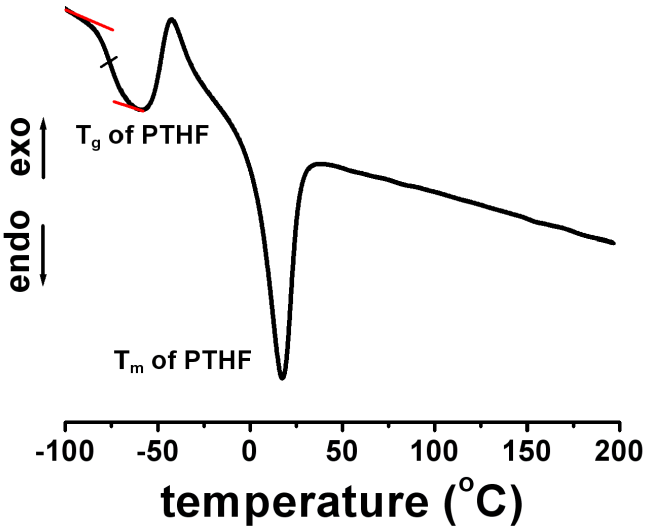

Fig. S10 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V2k-89 (89 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 2170 g/mol (heating rate = 10 °C/min).

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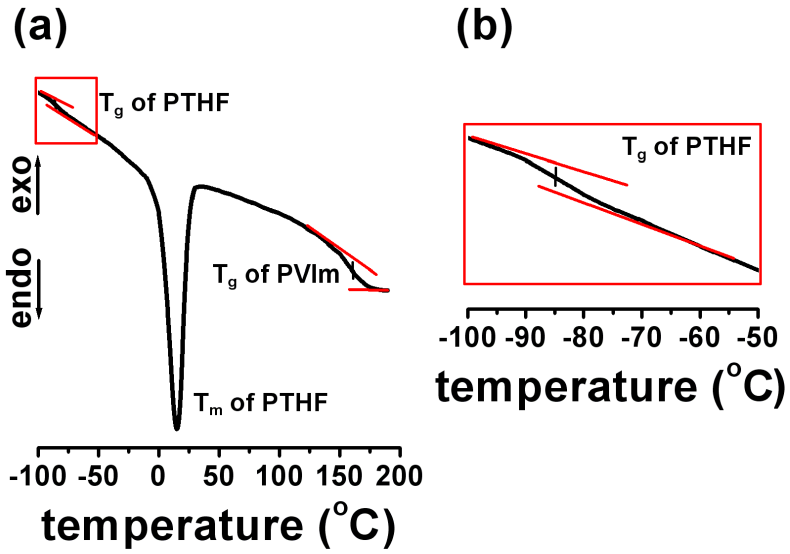

Fig. S11 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-52 (52 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 6850 g/mol (a) and enlargement of the thermogram in the -100 to -50 °C temperature range (b) (heating rate = 10 °C/min).

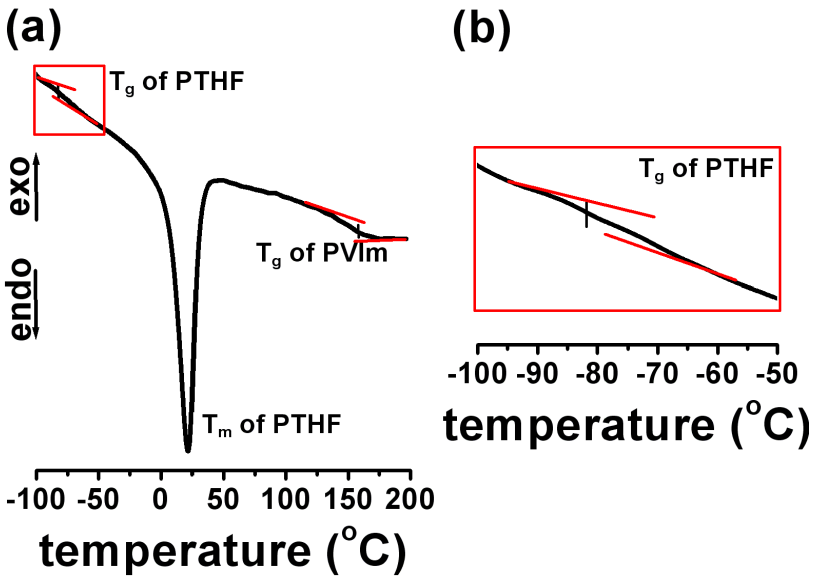

Fig. S12 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-61 (61 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 6850 g/mol (a) and enlargement of the thermogram in the -100 to -50 °C temperature range (b) (heating rate = 10 °C/min).

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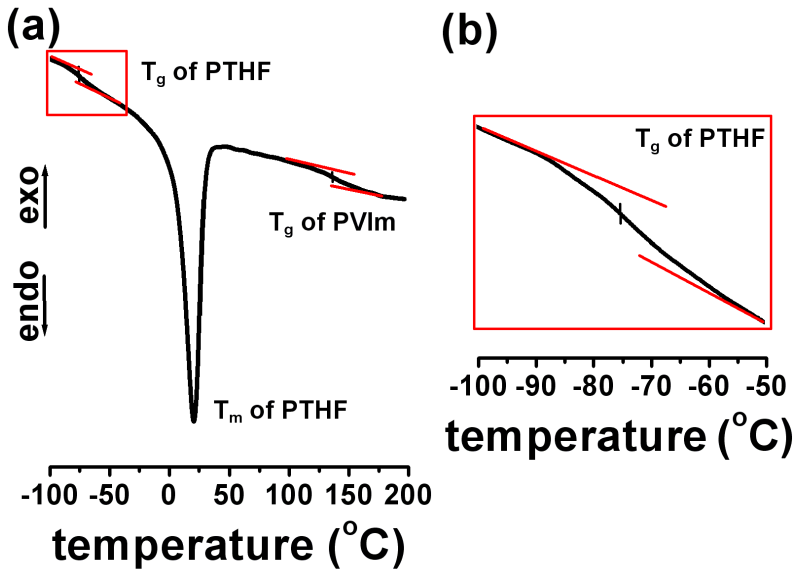

Fig. S13 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-69 (69 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 6850 g/mol (a) and enlargement of the thermogram in the -100 to -50 °C temperature range (b) (heating rate = 10 °C/min).

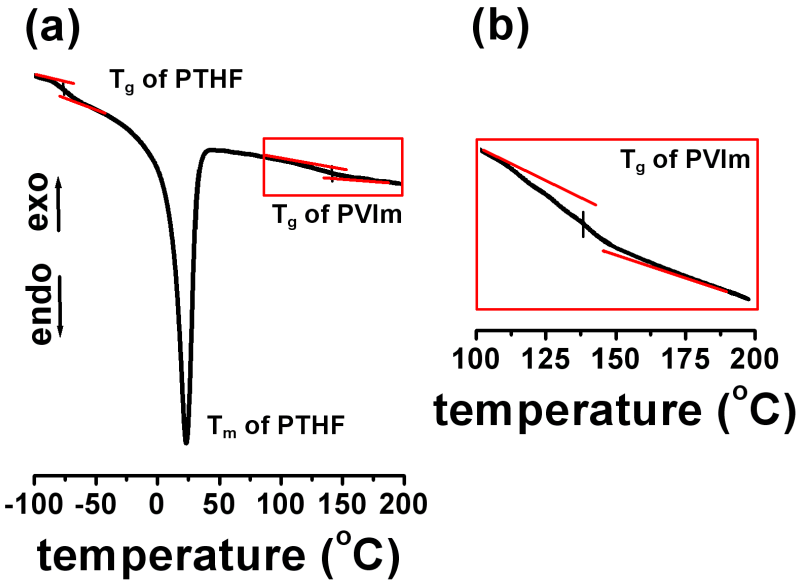

Fig. S14 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-80 (80 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 6850 g/mol (a) enlargement of the thermogram in the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

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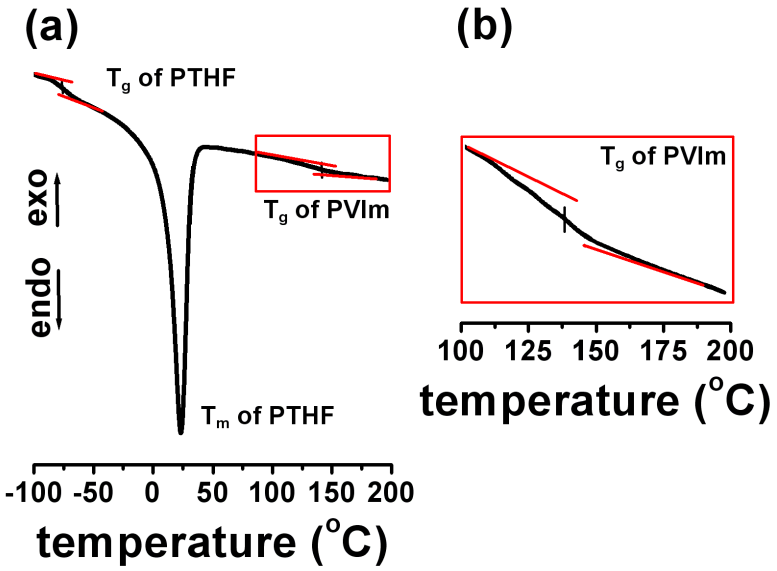

Fig. S15 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-81 (81 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 6850 g/mol (a) enlargement of the thermogram in the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

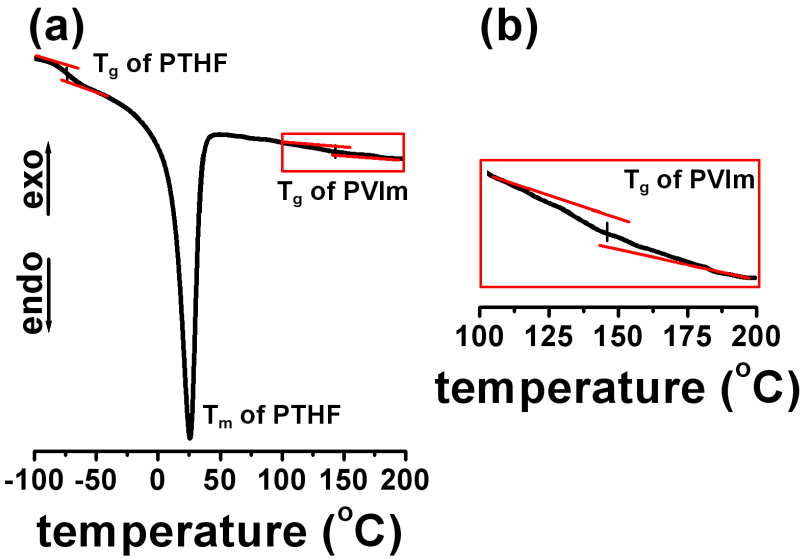

Fig. S16 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-84 (84 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 6850 g/mol (a) enlargement of the thermogram in the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

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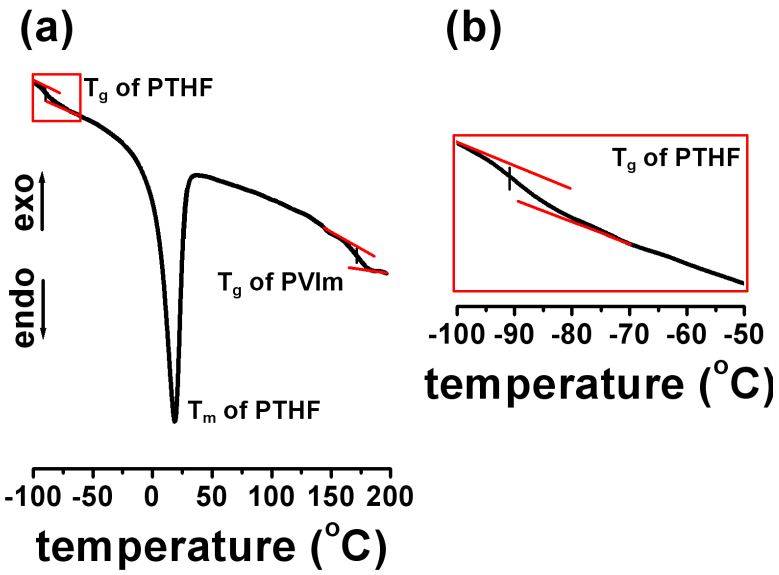

Fig. S17 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V10k-46 (46 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 10000 g/mol (a) and enlargement of the thermogram in the -100 to -50 °C temperature range (b) (heating rate = 10 °C/min).

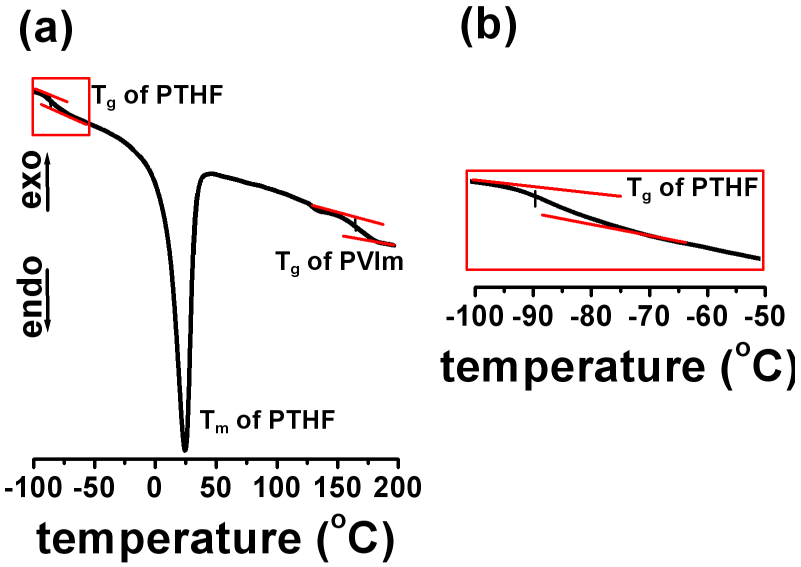

Fig. S18 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V10k-61 (61 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 10000 g/mol (a) and enlargement of the thermogram in the100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

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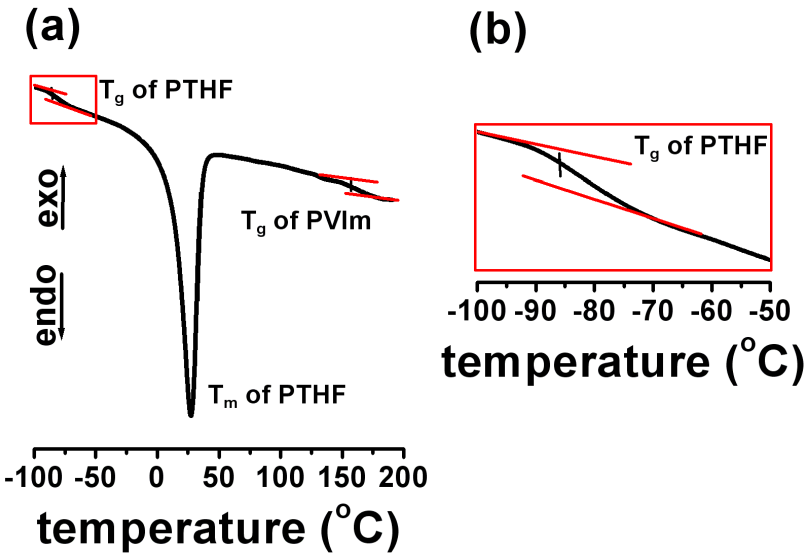

Fig. S19 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-62 (62 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 6850 g/mol (a) enlargement of the thermogram in the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

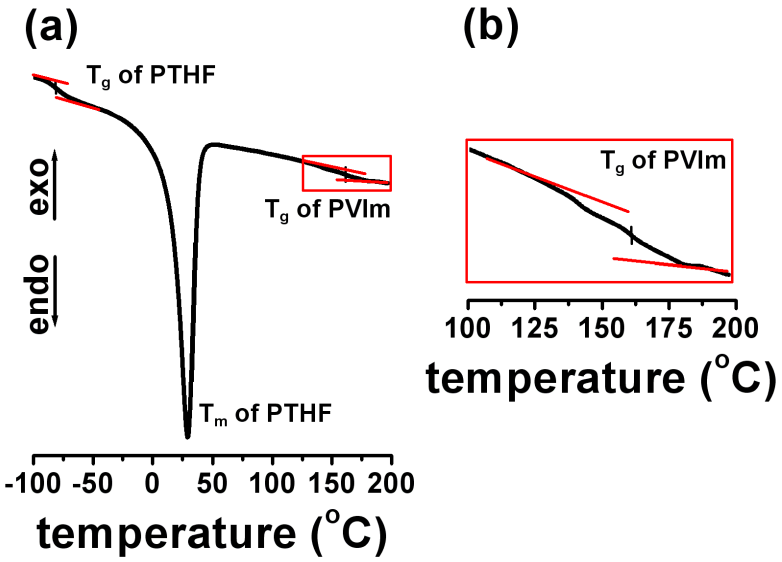

Fig. S20 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V10k-77 (77 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 10000 g/mol (a) and enlargement of the thermogram in the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

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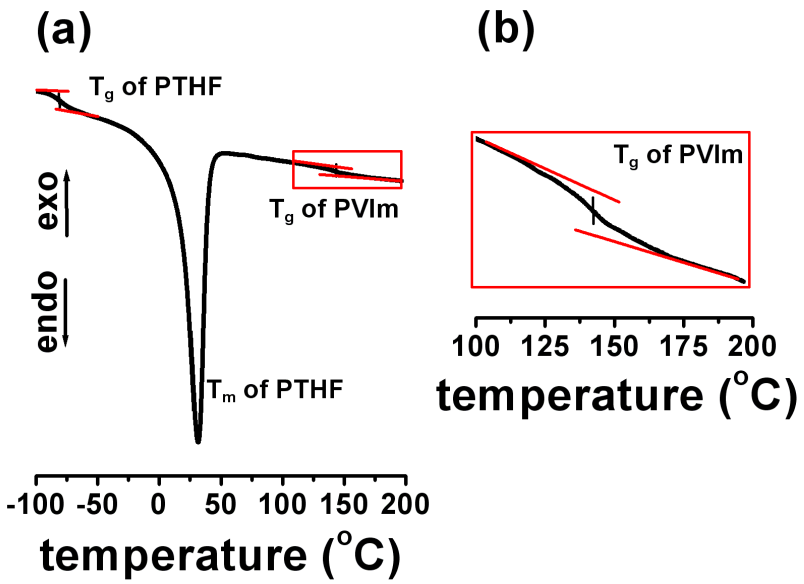

Fig. S21 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V10k-86 (86 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 10000 g/mol (a) and enlargement of the thermogram in the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

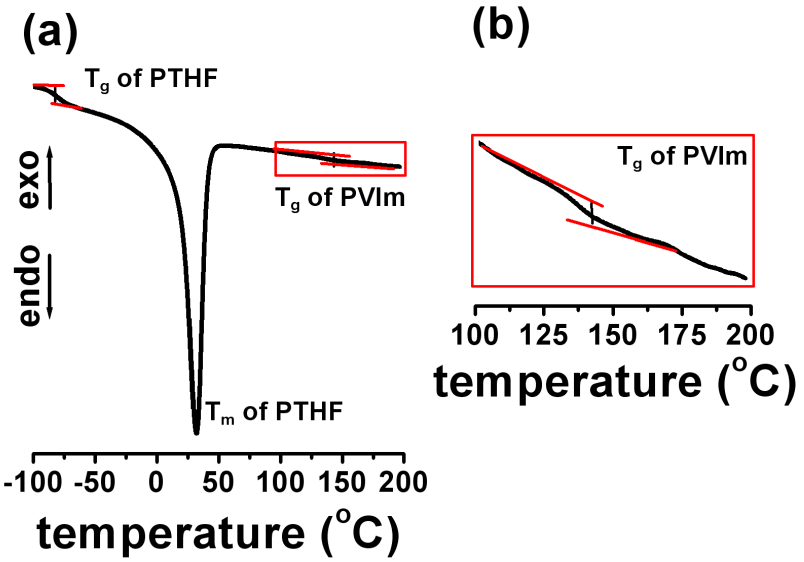

Fig. S22 Differential scanning calorimetry (DSC) thermogram (second heating scan) of V10k-91 (91 wt% PTHF) PVIm-*l*-PTHF conetwork, containing PTHFDMA with M_n of 10000 g/mol (a) and enlargement of the thermogram in the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).

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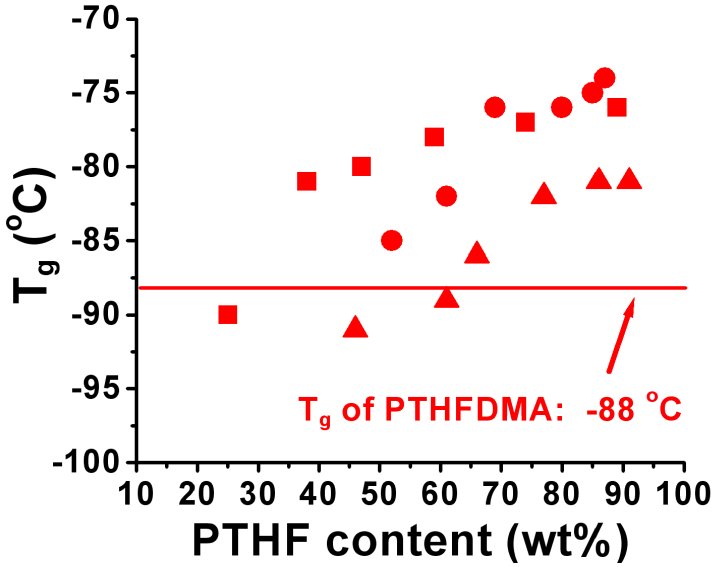

Fig. S23 Glass transition temperature (T_g) values of the poly(tetrahydrofuran) (PTHF) component of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks as a function of composition ((■) V2k, (●) V7k, (▲) V10k PVIm-*l*-PTHF series, and the line represents the T_g of the PTHFDMA macromolecular cross-linker).

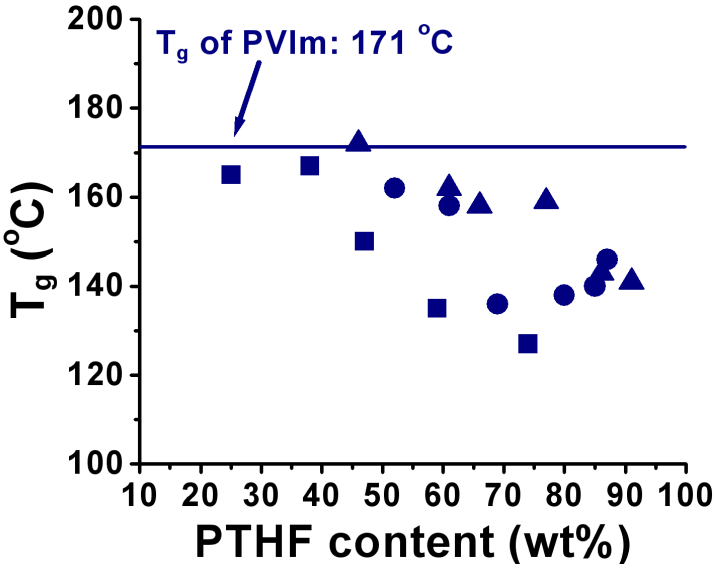

Fig. S24 Glass transition temperature (T_g) values of the poly(*N*-vinylimidazole) (PVIm) component of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks as a function of composition ((■) V2k, (●) V7k, (▲) V10k PVIm-*l*-PTHF series, and the line represents the T_g of the PVIm homopolymer).

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Table S2 Compositions, melting points, crystalline fractions (X_c) and glass transition temperatures (T_g) of blends consist of poly(*N*-vinylimidazole) (PVIm) and poly(tetrahydrofuran) with varying molecular weights (see Experimental for sample identification).

Sample code	PVIm/PTHF in blend (wt %)	T_m (°C)	X_c (%)	T_g (PTHF) (°C)	T_g (PVIm) (°C)
PVIm	--	--	--	--	171
PTHFDMA2k	--	23	47.1	-87	--
PTHFDMA7k	--	28	60.4	-89	--
PTHFDMA10k	--	30	75.4	-89	--
B2k-90	10/90	22	45.2	-87	172
B2k-80	20/80	22	45.7	-87	171
B2k-50	50/50	23	52.4	-85	173
B7k-50	50/50	26	63.2	-88	172
B10k-50	50/50	29	69.4	-89	165

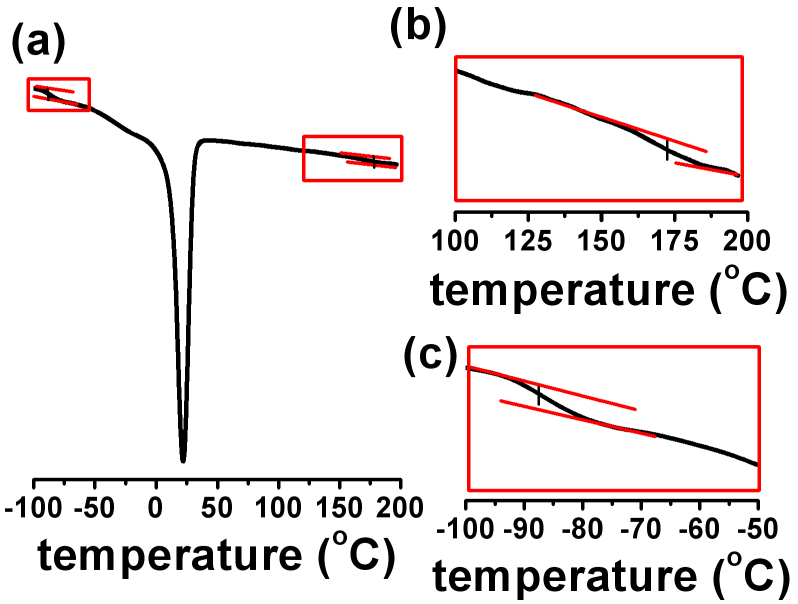

Fig. S25 Differential scanning calorimetry (DSC) thermogram (second heating scan) of B2k-90 (PVIm:PTHF 10:90 wt%) blends of poly(tetrahydrofuran) and poly(*N*-vinylimidazole) homopolymers, containing PTHFDMA with M_n of 2170 g/mol (a) enlargement of the thermogram in the 100 to 200 °C temperature range (b) and enlargement of the thermogram in the -100 to -50 °C temperature range (c) (heating rate = 10 °C/min).

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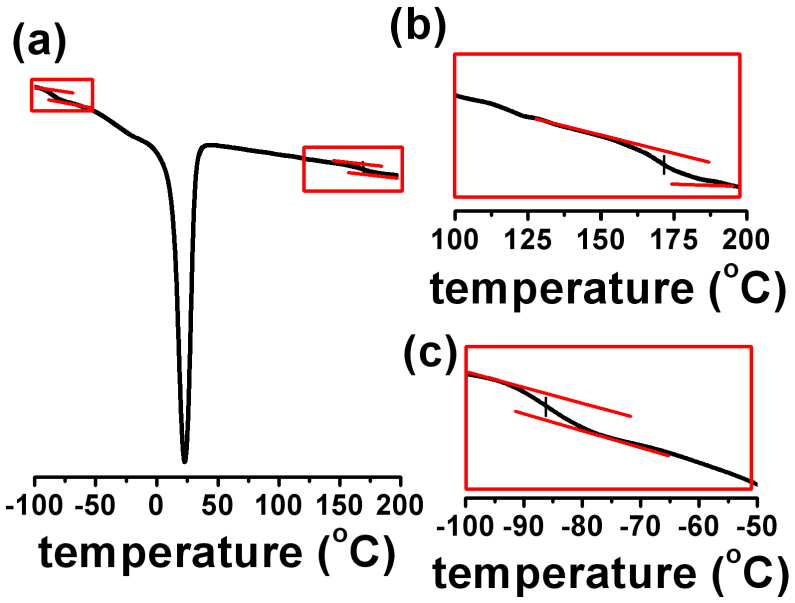

Fig. S26 Differential scanning calorimetry (DSC) thermogram (second heating scan) of B2k-80 (PVIm:PTHF 20:80 wt%) blends of poly(tetrahydrofuran) and poly(*N*-vinylimidazole) homopolymers, containing PTHFDMA with M_n of 2170 g/mol (a) enlargement of the thermogram in the 100 to 200 ^{o}C temperature range (b) and enlargement of the thermogram in the -100 to -50 ^{o}C temperature range (c) (heating rate = 10 °C/min).

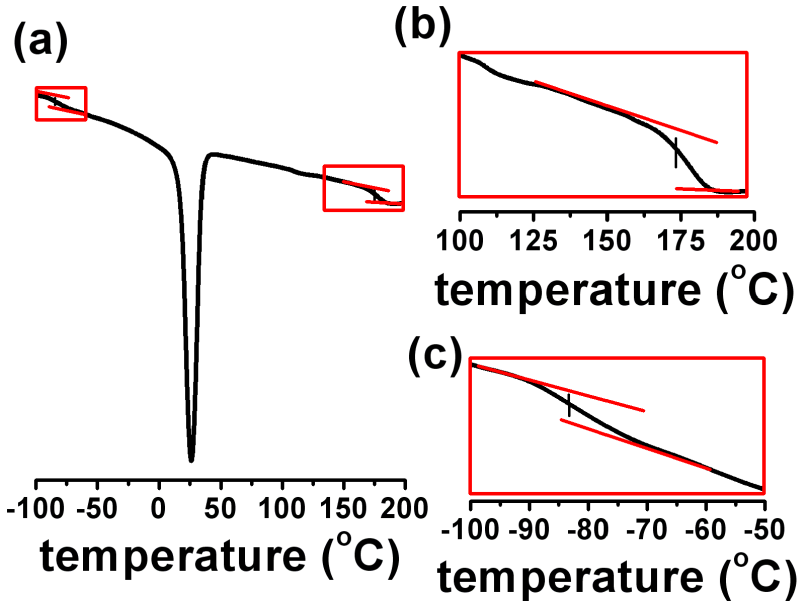

Fig. S27 Differential scanning calorimetry (DSC) thermogram (second heating scan) of B2k-50 (PVIm:PTHF 50:50 wt%) blends of poly(tetrahydrofuran) and poly(*N*-vinylimidazole) homopolymers, containing PTHFDMA with M_n of 2170 g/mol (a) enlargement of the thermogram in the 100 to 200 ^{o}C temperature range (b) and enlargement of the thermogram in the -100 to -50 ^{o}C temperature range (c) (heating rate = 10 °C/min).

ELECTRONIC SUPPLEMENTARY INFORMATION

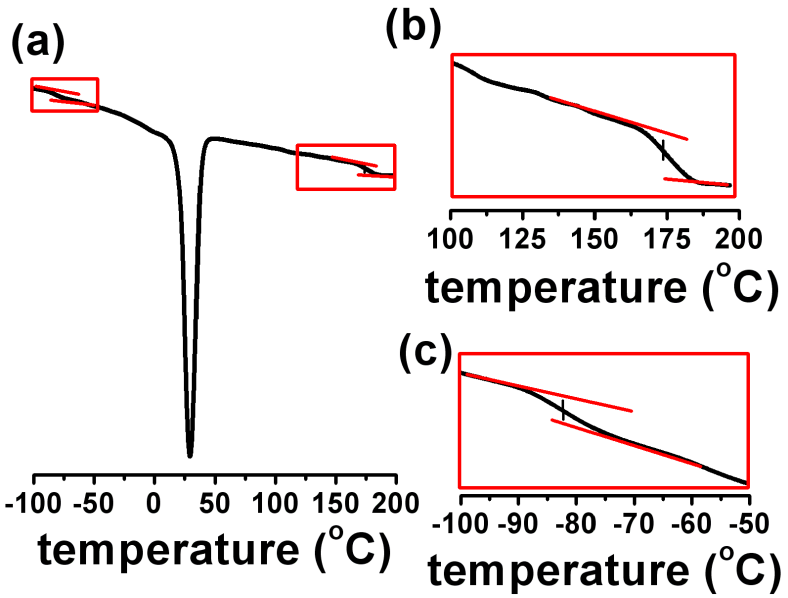

Fig. S28 Differential scanning calorimetry (DSC) thermogram (second heating scan) of B7k-50 (PVIm:PTHF 50:50 wt%) blends of poly(tetrahydrofuran) and poly(*N*-vinylimidazole) homopolymers, containing PTHFDMA with M_n of 6850 g/mol (a) enlargement of the thermogram in the 100 to 200 ^{o}C temperature range (b) and enlargement of the thermogram in the -100 to -50 ^{o}C temperature range (c) (heating rate = 10 °C/min).

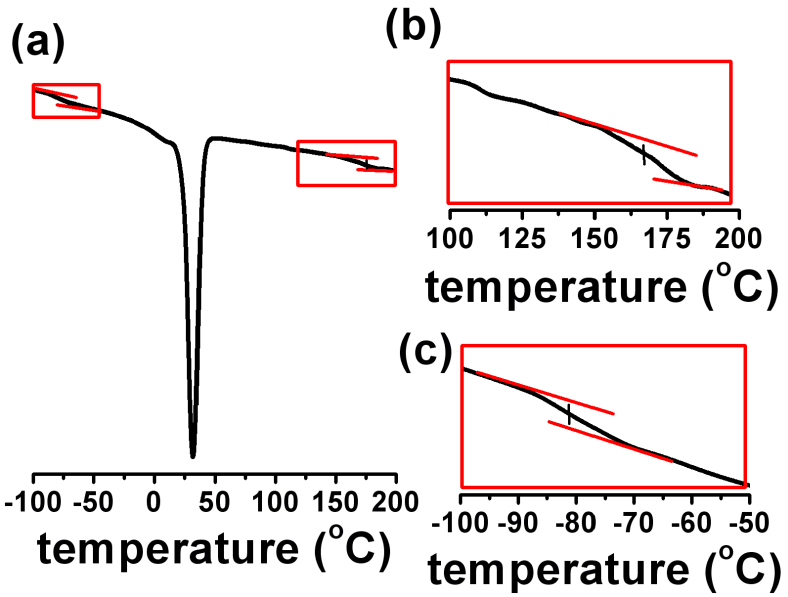

Fig. S29 Differential scanning calorimetry (DSC) thermogram (second heating scan) of B10k-50 (PVIm:PTHF 50:50 wt%) blends of poly(tetrahydrofuran) and poly(*N*-vinylimidazole) homopolymers, containing PTHFDMA with M_n of 10000 g/mol (a) enlargement of the thermogram in the 100 to 200 ^{o}C temperature range (b) and enlargement of the thermogram in the -100 to -50 ^{o}C temperature range (c) (heating rate = 10 °C/min).

ELECTRONIC SUPPLEMENTARY INFORMATION

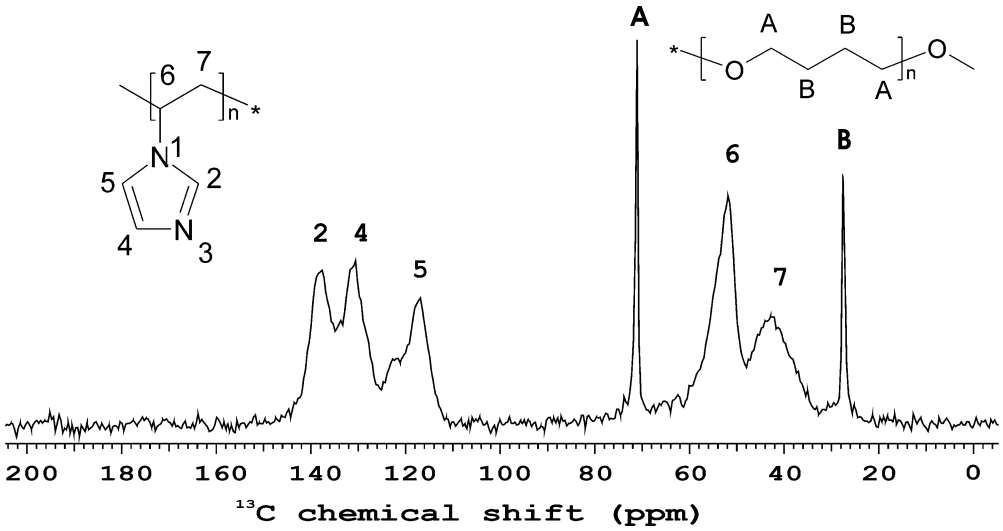

Fig. S30 Cross polarization magic angle spinning spectra of V7k-52 poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) sample at 40 ^{o}C with contact time of 2ms. The spinning speed was 8 kHz.

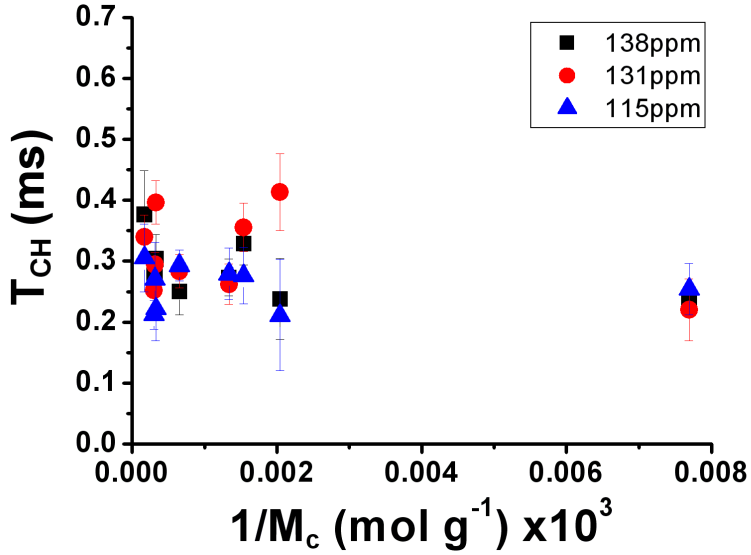

Fig. S31 Time coefficient of the cross polarization (T_{CH}) of the aromatic carbons of the poly(*N*-vinylimidazole) phase at 40 ^{o}C as a function of the average molecular weights of the hydrophilic PVIm segments between two cross-linking points (M_c) in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks.

ELECTRONIC SUPPLEMENTARY INFORMATION

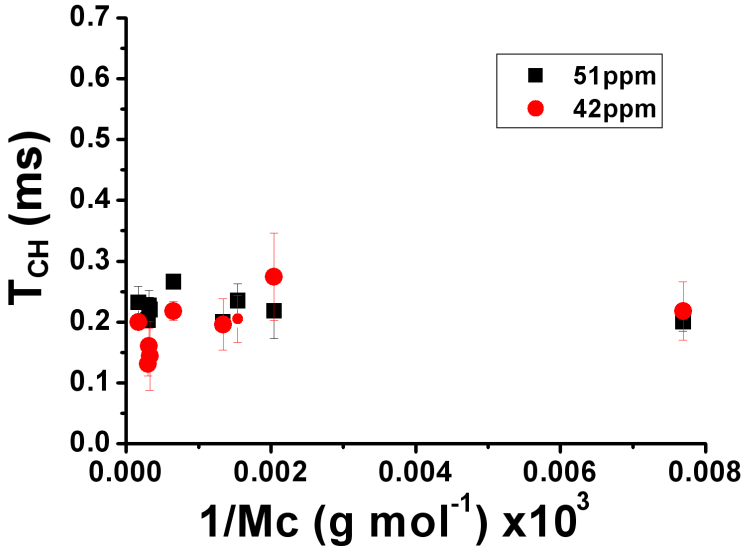

Fig. S32 Time coefficient of the cross polarization (T_{CH}) of the aliphatic carbons of the poly(*N*-vinylimidazole) phase at 40 ^{o}C as a function of the average molecular weights of the hydrophilic PVIm segments between two cross-linking points (M_c) in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks.