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) (PTHFDMA) with methacryloyl chloride. The synthesis of the higher molecular weight dimethacrylate terminated poly(tetrahydrofuran)s (PTHFDMA) macromonomers have been obtained by cationic ring opening polymerization of tetrahydrofuran (THF) by initiation with trifluoromethanesulfonic anhydride (Tf\(_2\)O) 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\(_2\)O (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.
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$_{1\text{trans}}$; m), 6.09 (1H; H$_{1\text{cis}}$; m)
ELECTRONIC SUPPLEMENTARY INFORMATION

(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 °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 °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.
**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 (Mn 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).
**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).
**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).
**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).
**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).
**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).
**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).
**Fig. S15** Differential scanning calorimetry (DSC) thermogram (second heating scan) of V7k-81 (81 wt% PTHF) PVIm-1-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-1-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. 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 the 100 to 200 °C temperature range (b) (heating rate = 10 °C/min).
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).
**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).
**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).
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).

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<th>$X_c$ (%)</th>
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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 $^\circ$C temperature range (b) and enlargement of the thermogram in the -100 to -50 $^\circ$C temperature range (c) (heating rate = 10 $^\circ$C/min).
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 °C temperature range (b) and enlargement of the thermogram in the -100 to -50 °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 °C temperature range (b) and enlargement of the thermogram in the -100 to -50 °C temperature range (c) (heating rate = 10 °C/min).
**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 Mₙ of 6850 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).

**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 Mₙ of 10000 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).
**Fig. S30** Cross polarization magic angle spinning spectra of V7k-52 poly(N-vinylimidazole)-l-poly(tetrahydrofuran) (PVIm-l-PTHF) sample at 40 °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 °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.
Fig. S32 Time coefficient of the cross polarization (T_{CH}) of the aliphatic carbons of the poly(N-vinylimidazole) phase at 40 °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.