Electronic Supplementary Material (ESI) for RSC Advances.

ELECTRONIC SUPPLEMENTARY INFORMATION

Unexpected Thermal Decomposition Behavior of Poly(*N*-vinylimidazole)-*l*-Poly(tetrahydrofuran) Amphiphilic Conetworks, a Class of Chemically Forced Blends

Csaba Fodor[*a], *János Bozi*[b], *Marianne Blazsó*[b] *and Béla Iván*[a]

[a]Polymer Chemistry Group and [b]Renewable and Clean Energy Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Hungary

*Corresponding author
E-mail: fodor.csaba@ttk.mta.hu (Csaba Fodor)

For comparison with the conetworks, polymer blends composed of poly(*N*-vinylimidazole) (PVIm) homopolymer and poly(tetrahydrofuran) dimethacrylate (PTHFDMA) macromonomer with different weight ratios and with different molecular weights of PTHFDMA were prepared by solvent casting from common solvent of ethanol (Table S1) to investigate the thermal behavior and stability of the not cross-linked immiscible polymer systems (Figure S1-2 and TableS2).

Table S1. Weight ratios of blends of poly(*N*-vinylimidazole) (PVIm) homopolymer and poly(tetrahydrofuran) dimethacrylate (PTHFDMA) macromonomers with different molecular weights (M_n = 4760, 6850, 10000 g/mol) and with different PVIm/PTHFDMA ratios (25, 50, 75 wt% of PTHFDMA).

Sample	PVIm/PTHF ratio (w/w%)	M_n(PTHFDMA) (g/mol)	m(PVIm) (g)	m(PTHFDMA) (g)	m(blend) (g)	V(EtOH) (ml)
B4.8k-25	75/25	4800	0.1492	0.0516	0.2008	3
B4.8k-50	50/50	4800	0.1040	0.1126	0.2166	3
B4.8k-75	25/75	4800	0.0503	0.1438	0.1941	3
B6.9k-25	75/25	6900	0.1503	0.0545	0.2048	3
B6.9k-50	50/50	6900	0.1014	0.0976	0.1990	3
B6.9k-75	25/75	6900	0.0509	0.1479	0.1988	3
B10k-25	75/25	10000	0.1478	0.0510	0.1988	3
B10k-50	50/50	10000	0.1036	0.1070	0.2106	3
B10k-75	25/75	10000	0.0520	0.1563	0.2083	3

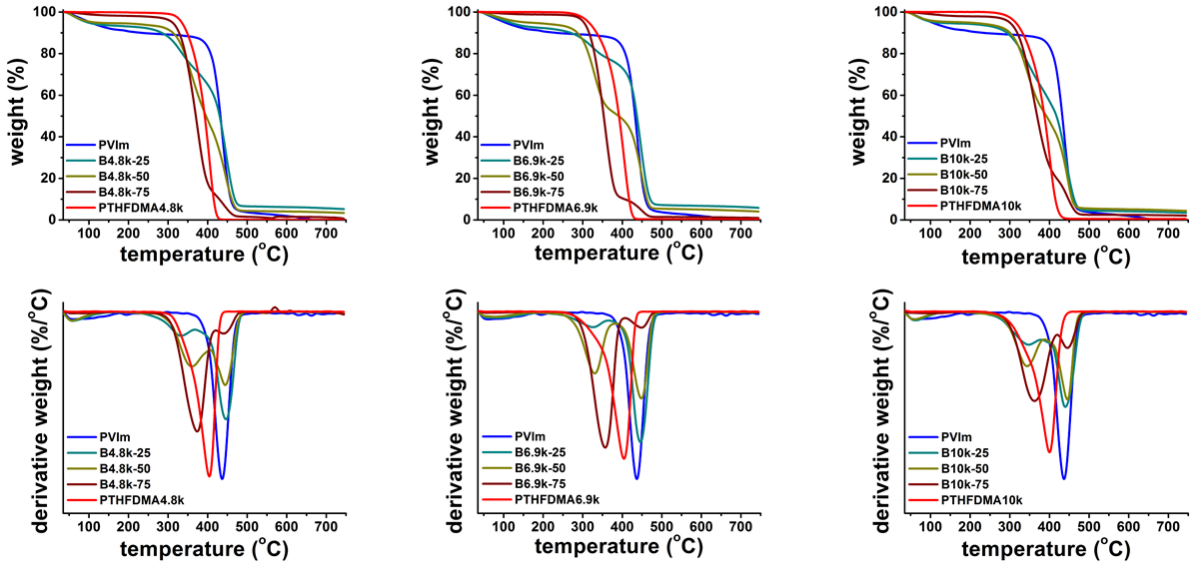

Figure S1. Thermogravimetric analysis (TG) (mass loss and derivative (DTG) curves) of blends of poly(*N*-vinylimidazole) (PVIm) homopolymer and poly(tetrahydrofuran) dimethacrylate (PTHFDMA) macromonomers (M_n = 4760, 6850, 10000 g/mol) and with different PVIm:PTHFDMA ratios (25, 50, 75 wt% of PTHFDMA).

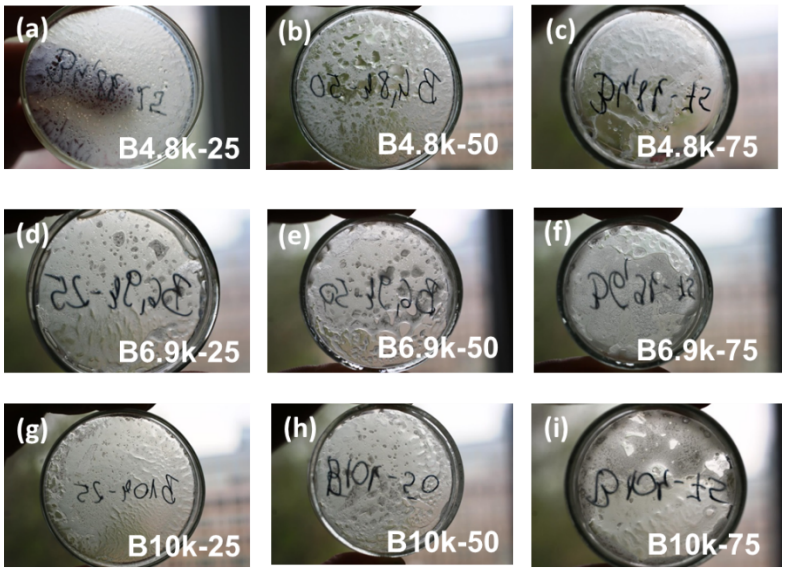

Figure S2. Photographs of blends of poly(*N*-vinylimidazole) (PVIm) homopolymer and poly(tetrahydrofuran) dimethacrylate (PTHFDMA) macromonomers with different molecular weights (M_n = 4760, 6850, 10000 g/mol) and with different PVIm/PTHFDMA weight ratios (see Table S1 for sample identification).

Table S2. Characteristic thermal decomposition data of poly(*N*-vinylimidazole) (PVIm) homopolymer, poly(tetrahydrofuran) dimethacrylate (PTHFDMA) macromonomerts, their poly(*N*-vinylimidazole)/poly(tetrahydrofuran) (PVIm/PTHF) blends (only for the two major decomposition transitions corresponding to the pure polymers without the solvent evaporation and final decomposition steps), and their char yields (Y_c).

Sample	T_{d1} (°C)	T_{d2} (°C)	Y_c (%)	Y_c(PVIm) (%)
PVIm	145*	446	3.7	5.6
PTHFDMA4.8k	407	-	0.0	0.0
PTHFDMA6.9k	406	-	0.2	0.2
PTHFDMA10k	402	-	0.5	0.5
B4.8k-75	379	448	0.6	2.5
B4.8k-50	361	446	3.3	7.0
B4.8k-25	333	447	5.2	7.5
B6.9k-75	358	450	0.9	3.7
B6.9k-50	332	448	4.0	8.6
B6.9k-25	325	446	5.8	8.5
B10k-75	364	449	2.0	8.2
B10k-50	346	448	4.3	9.2
B10k-25	345	431	3.4	4.9

T_{dx} (°C): temperature of maximum rate of weight loss
Y_c (%): char yield at 500°C
Y_c(PVIm) (%): char yield related to PVIm content at 500°C
*: evaporation of residual solvents

Thermogravimetric (TG), differential thermogravimetric (DTG) (Figures S3 and S4), and TG-MS molecular ion curves (Figures S4) of the homopolymer blends and the conetworks in the same composition range were compared, and the decomposition of the homopolymers in these mixtures (blends) only slightly differs from the decomposition of the pure homopolymers.

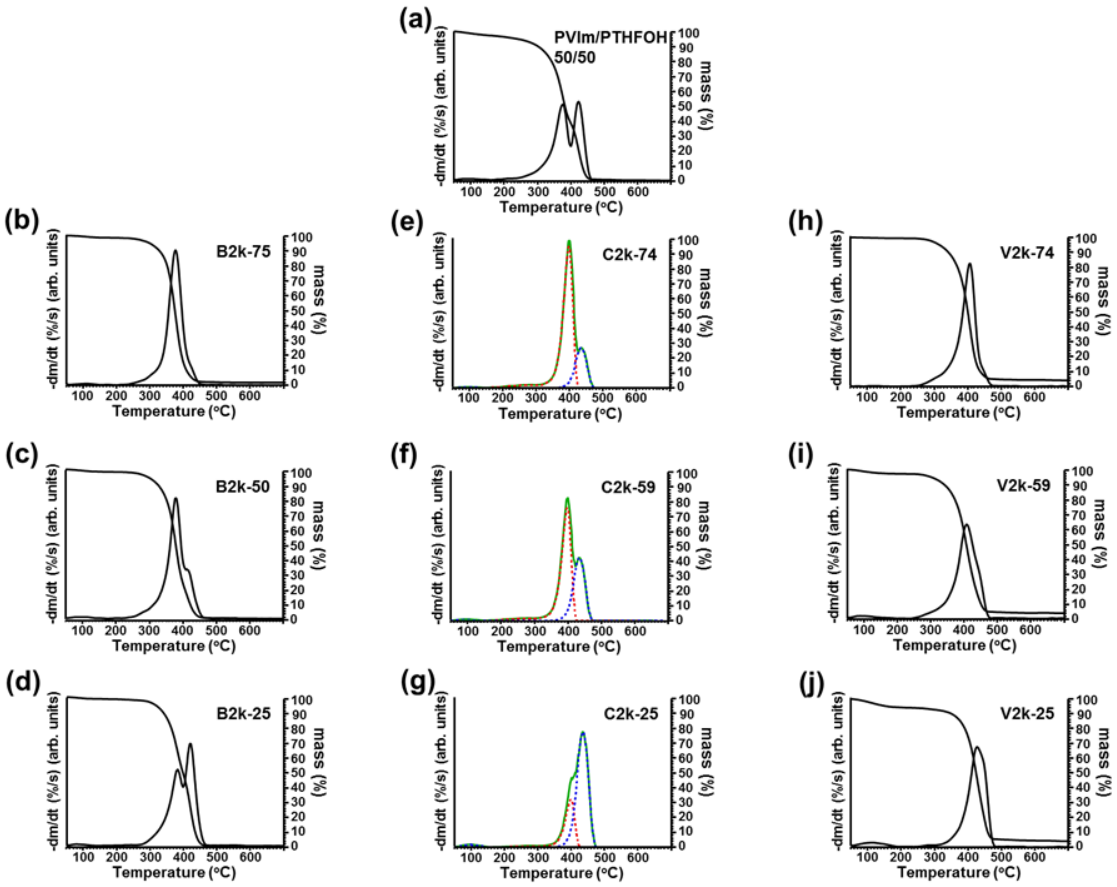

Figure S3. Thermogravimetric analysis (TG), differential thermogravimetric (DTG) curves of blend of poly(N-vinylimidazole) (PVIm) and dihydoxy-poly(tetrahydrofuran) (PTHFDOH) (M_n = 2000 g/mol) homopolymers with PVIm/PTHFDOH 1:1 content (a), blends of poly(*N*-vinylimidazole) (PVIm) and poly(tetrahydrofuran)dimethacrylate with different PVIm:PTHFDMA ratios of 75wt% (b), 50 wt% (c), 25 wt% (d) of PTHFDMA (M_n = 2200 g/mol); calculated DTG curves of samples with 74wt% (e), 59 wt% (f), 25 wt% (g) of PTHF (calculated DTG line of conetwork: green line, measured DTG curve of PTHF: red line; measured DTG line of PVIm: blue line); TG and DTG results of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks containing 74 wt% (h), 59 wt% (i) 25 wt% (j) PTHFDMA (M_n = 2200 g/mol) cross-linker.

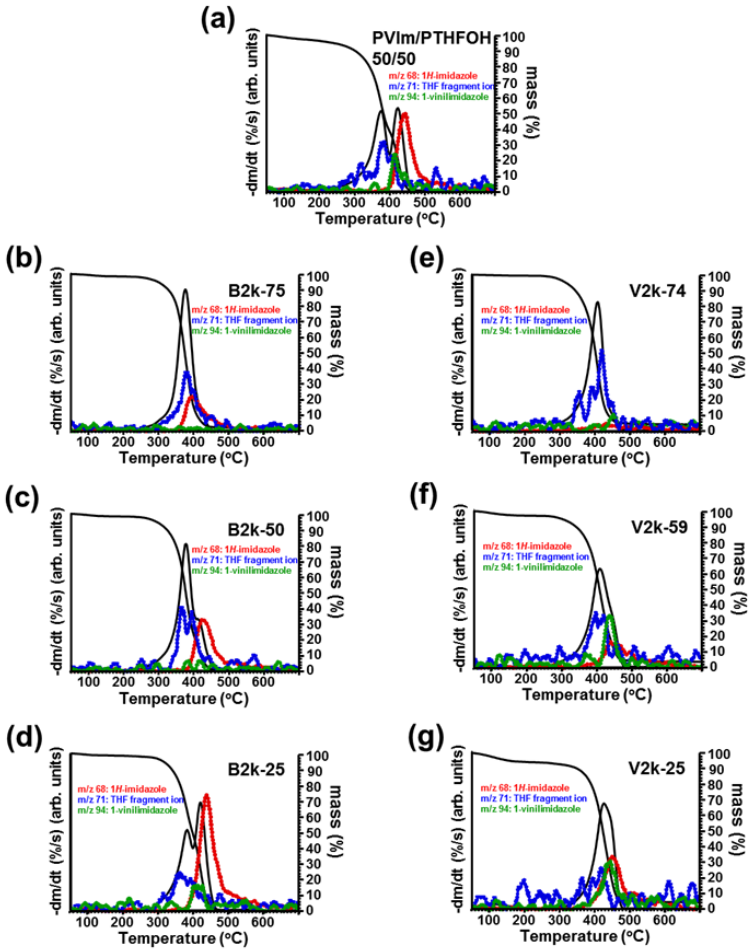

Figure S4. Thermogravimetric (TG), differential thermogravimetric (DTG), and TG-MS molecular ion curves of poly(*N*-vinylimidazole)/poly(tetrahydrofuran)-dihydroxy blend (with PVIm/PTHF 1:1 content) (a), poly(*N*-vinylimidazole)/poly(tetrahydrofuran)-dihydroxy (PVIm/PTHF belnds) with different PVIm:PTHF ratios 75wt% (b), 50wt% (c), 25wt% (d) of PTHFDMA and poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) conetworks containing 74 wt% (e), 59 wt% (f) 25 wt% (g) of PTHFDMA cross-linker (Mn = 2200). Mass loss and DTG curves: solidlines; TG-MS characteristic fragment ion of THF (m/z 71): blue; molecular ion curve of 1*H*-imidazole (m/z 68): green; molecular ion curve of 1-vinylimidazole (m/z 94): red.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) measurement (flash pyrolysis method was applied at 500 °C) were made on the PTHF polymers with different endgroups (Figure S5-S7)

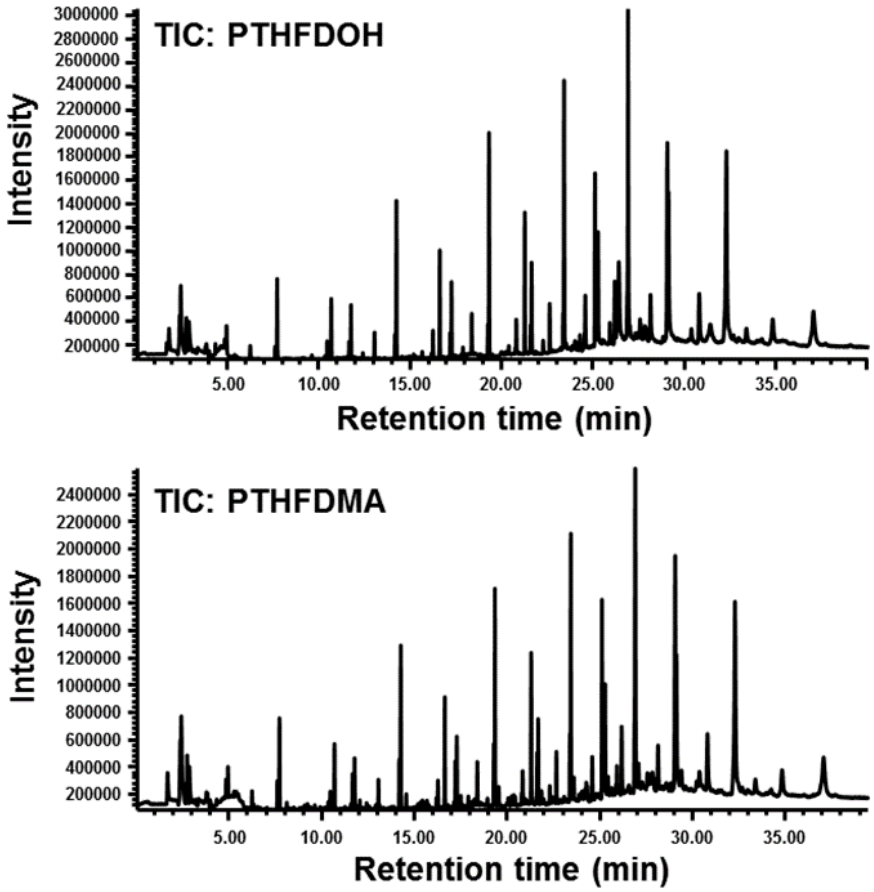

Figure S5. Pyrolysis-GC/MS total ion chromatograms of PTHF (upper) and PTHFDMA (lower).

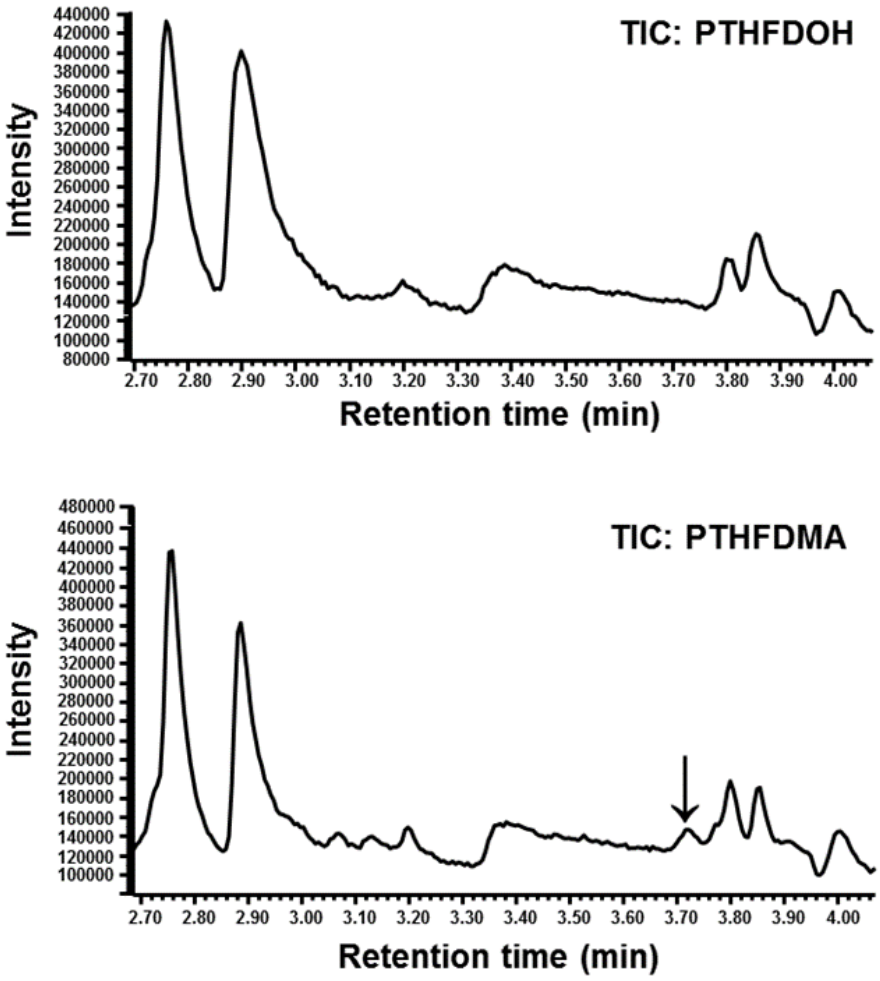

Figure S6. Volatile segment of the GC/MS total ion chromatograms of pyrolysis products of PTHF (upper) and PTHFDMA (lower), and the GC/MS identification of the small peak of methacrylic acid is indicated by an arrow.

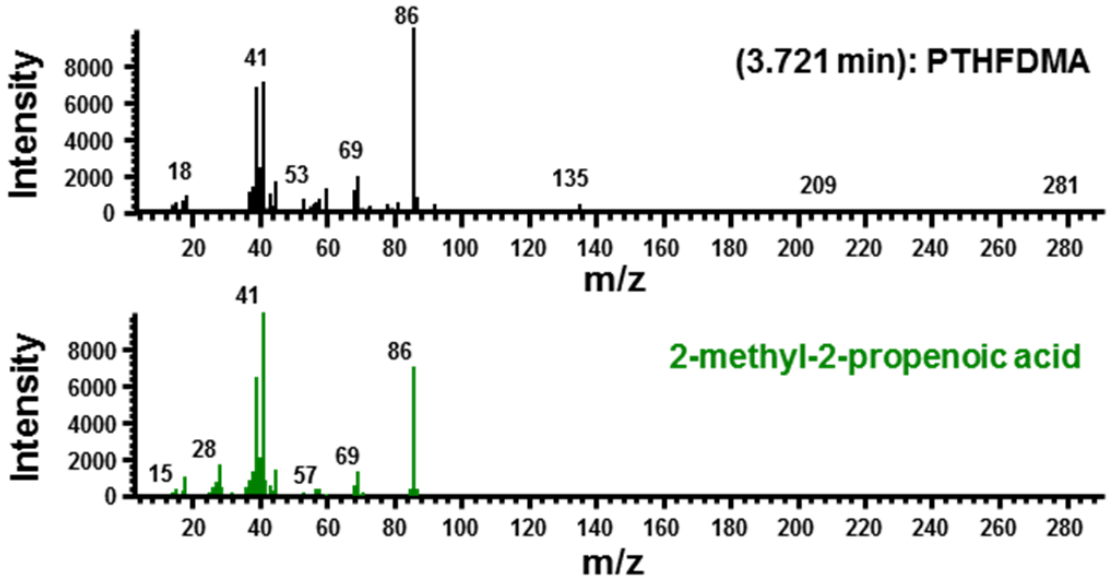

Figure S7. *NIST* identification of 2-methyl-2-propenoic acid at 7.721 retention time.

To study the thermal processes and reactions, measured and calculated DTG curves of the PVIm-*l*-PTHF conetworks were compared (Figure S8) to show the differences between the measured and calculated DTG curves of the conetworks.

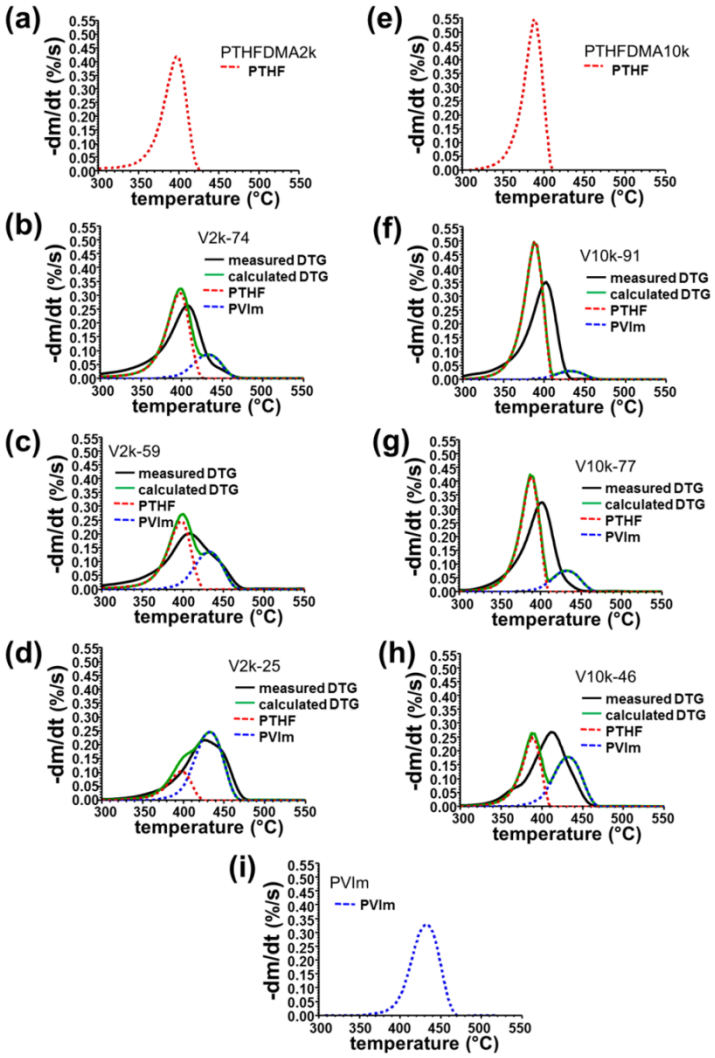

Figure S8. Differential thermogravimetric (DTG) curves of the PTHFDMA cross-linker (M_n = 2200) (a), poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks containing 74 wt% (b), 59 wt% (c) 25 wt% (d) containing PTHFDMA with M_n = 2200, PTHFDMA cross-linker with M_n = 10000 (e), PVIm-*l*-PTHF conetworks containing 91 wt% (f), 77 wt% (g) 46 wt% (h) with PTHFDMA of M_n = 10000, and PVIm homopolymer (i). Measured DTG curve of PTHF: red line; measured DTG line of PVIm: blue line; measured DTG line of conetwork: black line; calculated DTG line of conetwork: green line.

Char formation is generally monitored with TG-MS ion curves of H_2^+ molecule (m/z = 2) and CH_3^+ (m/z = 15). Thermal decomposition of PTHFDMA takes place without char formation. On the other hand, for both PVIm and the conetworks enhanced char formation can be seen in the temperature domain of 500-700 °C (Figure S9).

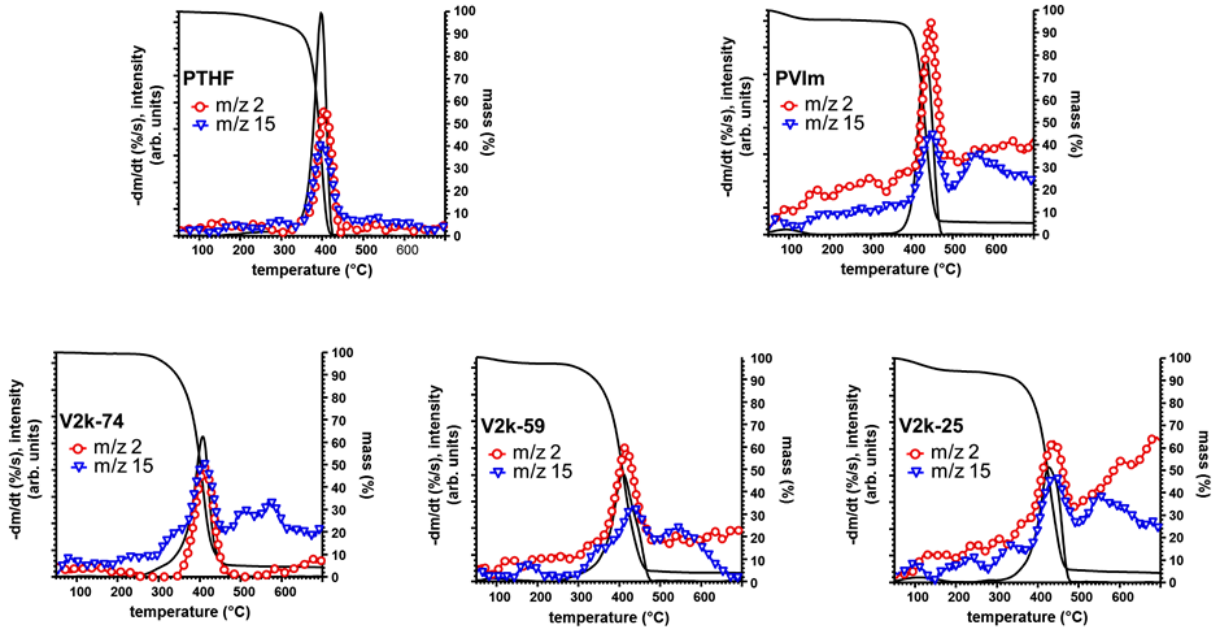

Figure S9. Thermogravimetric (TG) and TG-MS ion curves of hydrogen (m/z = 2, blue line) and methane (m/z = 15, red line) of the macromolecular PTHFDMA cross-linker with M_n = 2200 (a), poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks containing 74 wt% (b), 59 wt% (c) and 25 wt% (d) PTHF, and PVIm homopolymer (e).

The thermal stability and decomposition of the B2k-25 poly(*N*-vinylimidazole)/poly(tetrahydrofuran) (PVIm/PTHF) blend (with PVIm/PTHF of 3:1 content) were studied by TG-MS in inert atmosphere. The results of the TG-MS molecular ion curves indicate separate thermal decomposition of the two components (PVIm and PTHF) in the blends (Figure S10a and S10b).

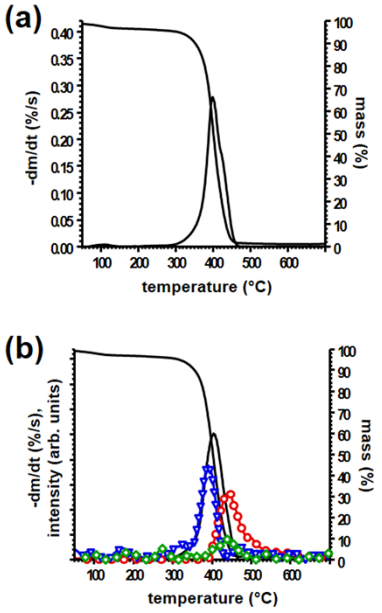

Figure S10. Thermogravimetric (TG), differential thermogravimetric (DTG), and TG-MS molecular ion curves of B2k-25 (with PVIm/PTHF 3:1 content) poly(*N*-vinylimidazole)/poly(tetrahydrofuran) (PVIm/PTHF) homopolymer blend thermal decomposition in inert argon atmosphere (a) and the respective molecular ion curves (b). Mass loss and DTG curves: full line; TG-MS molecular ion curve of 1*H*-imidazole (*m/z* = 68, red line); characteristic fragment ion of THF and its oligomers (*m/z* = 71, blue line); molecular ion curve of THF (*m/z* =72, green line).