

# 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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Unexpected correlations have been found between structural parameters and glass transition temperatures ( $T_g$ ) of poly(*N*-vinylimidazole) (PVI<sub>m</sub>) and crystallinity of poly(tetrahydrofuran) (PTHF) in a series of novel, unique PVI<sub>m</sub>-*l*-PTHF amphiphilic conetworks synthesized in broad composition ranges via free radical copolymerisation of VIm and semicrystalline, methacrylate-telechelic PTHF macromolecular cross-linkers with varying  $M_n$  from 2170 to 10000 g/mol. Differential scanning calorimetry (DSC) investigations revealed microphase separation between the covalently bonded PVI<sub>m</sub> and PTHF components, that is two distinct  $T_g$ s corresponding to the respective polymers (PVI<sub>m</sub> and PTHF) were obtained in these optically clear, transparent materials. Complete microphase separation, i. e. absence of mixed phases was also confirmed by solid state NMR measurements. The  $T_g$  of the PVI<sub>m</sub> phase significantly decreases with increasing PTHF content, and Fox-Flory type correlation was surprisingly found between the  $T_g$  of PVI<sub>m</sub> and its  $M_c$  (average molecular weight between cross-links). This striking finding indicates a unique, unpredicted *scissor effect* of the macromolecular PTHF cross-linker in these materials, i. e. in respect of glass transition, PVI<sub>m</sub> behaves as individual chain between cross-links. The molecular mobility in the PVI<sub>m</sub> chain segments obtained by solid state NMR investigations shows similar trend as a function of  $M_c$ . In the DSC thermograms, the semicrystalline PTHF has sharp endothermic melting peak ( $T_m$ ) indicating partial crystallisation of this polymer. It was found that the  $T_m$  and the crystalline fraction ( $X_c$ ) of the PTHF phase is suppressed by even the minimal content of PVI<sub>m</sub> phase in the conetworks. Even complete diminishing of  $X_c$  occurs in conetworks with lower than 40 wt% PTHF of the lowest  $M_n$  (2170 g/mol). Unexpectedly,  $T_m$  linearly decreases with  $M_c$  in conetworks with constant  $M_n$  of PTHF. These data indicate that the decrease of both  $T_m$  and  $X_c$  of PTHF is not only composition dependent, but the MW of the macromolecular PTHF cross-linker and the  $M_c$  of the PVI<sub>m</sub> component as well have effect on these parameters. These results also indicate that chemical bonding of polymer chains in conetworks yields novel materials with unprecedented property variation. This provides unique opportunities for fine tuning of the investigated fundamental material properties, i. e.  $T_g$ ,  $T_m$  and  $X_c$ , within certain ranges in the novel PVI<sub>m</sub>-*l*-PTHF amphiphilic conetworks by selecting the proper synthesis parameters, that is, composition and MW of the telechelic PTHF macromonomer cross-linker.

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## Introduction

Polymer conetworks, especially amphiphilic conetworks (APCNs), consisting of covalently, ionically or supramolecularly

bonded immiscible hydrophilic and hydrophobic cross-linked polymer chains belong to a novel class of cross-linked polymeric materials, and these macromolecular assemblies have received significant interest in recent years.<sup>1-15</sup> This is mainly due to their unique amphiphilic behavior,<sup>2</sup> nanostructured phase separated morphology,<sup>3</sup> and especially to a large variety of application possibilities, such as antifouling surfaces,<sup>4</sup> contact lenses,<sup>5</sup> tissue engineering scaffolds,<sup>6</sup> controlled drug release matrices,<sup>2a-b,7</sup> membranes for immunoisolation,<sup>8</sup> separation membranes,<sup>9</sup> biomaterials,<sup>1b,10</sup> pervaporation membranes,<sup>5e,11</sup> sensors,<sup>12</sup> supports for enhanced enzyme catalysis,<sup>13</sup> nanoreactors or nanotemplates of nanohybrids,<sup>3a,13e</sup> solid-phase extraction<sup>14</sup> and cell culture surfaces<sup>6b,10b</sup> etc.

Recently, we have accomplished a synthetic procedure for the preparation of a unique class of such materials, poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVI<sub>m</sub>-*l*-PTHF, “P”

stands for “linked by”) amphiphilic conetworks with broad composition range and with varying molecular weights of the PTHF macromolecular cross-linker.<sup>15</sup> In these novel conetworks, poly(tetrahydrofuran) (PTHF) is a hydrophobic semicrystalline polymer. This polymer is an important raw material for synthetic flexible rubber strings (elastane), and often used as soft segment in thermoplastic elastomers, such as polyurethanes (PURs), due to its elasticity.<sup>16</sup> PTHF-based PURs are also important biomaterials.<sup>16</sup> PTHF synthesized by cationic ring-opening polymerisation of tetrahydrofuran is also used as component of a variety of block copolymers.<sup>17</sup> Such PTHF containing materials are widely used in both research and development investigations and commercial materials, for instance in products being in contact with blood and tissue as breast implant coatings, catheters, prosthesis tubes and vascular grafts.<sup>18</sup> The advantageous surface properties and the good bio- and hemocompatibility of PTHF have also opened the doors to the application of PTHF as coating of artificial hearts and valves, ventricular assist device insulators, intra-aortic balloon pumps etc.<sup>18a-g</sup> Only few reports exist on APCNs and their certain properties based on copolymerisation of PTHF macromolecular cross-linker with some monomers, such as acrylic acid, acrylamide, methacrylic acid and *N*-isopropyl acrylamide.<sup>11,19,20</sup>

Imidazole, the pendant functional group of the thermally stable<sup>15a</sup> poly(*N*-vinylimidazole) (PVIIm) in the PVIIm-*l*-PTHF conetworks,<sup>15b-d</sup> and its derivatives are incorporated in many essential biomacromolecules (e.g. DNA, RNA, proteins) and biosystems, pharmaceutical compounds, agrochemicals, and a large number of ionic and polyionic liquids are also based on imidazolium salts.<sup>21</sup> Synthetic polymers based on imidazole and imidazole derivatives are applied in metal ion complexing membranes,<sup>22</sup> ion imprinted matrices,<sup>23</sup> gene delivery vectors,<sup>24</sup> catalysts and catalyst supports,<sup>25</sup> fuel cell membranes,<sup>26</sup> synzymes, i.e. synthetic polymer enzyme mimics<sup>27</sup> etc.

The combination of the widely used hydrophilic PVIIm cross-linked by the biocompatible, elastic, hydrophobic PTHF macromonomer in a network structure is expected to lead to novel materials with special structure and properties. Although large number of studies has been reported on the thermal properties (glass transition and crystallisation) of block and graft copolymers and polymer blends (see e.g. Ref. 28 and references therein), the basic thermal characteristics of APCNs with PVIIm as the hydrophilic and PTHF as the hydrophobic component to the best of our knowledge have not been reported yet. Since revealing the thermal behavior of a new class of materials is crucial for the understanding of its structure-property relations and for determining the limiting conditions for its potential applications, herein we report, for the first time, on the synthesis of a series of PVIIm-*l*-PTHF APCNs with different molecular weights of the PTHF macromolecular cross-linkers in a wide range of composition and on the unique results obtained in the course of our systematic investigations aiming at to reveal the correlations between the fundamental structural parameters, such as the composition, the molecular weight of the PTHF cross-linker and the molecular weight of the PVIIm segments between cross-links, of these novel conetworks and the glass transition temperatures of the components and the crystallisation behavior of the semicrystalline PTHF in the conetworks.

## Experimental

### Materials

*N*-Vinylimidazole (VIm, Aldrich) was distilled under reduced pressure from CaH<sub>2</sub> (Aldrich) at 72 °C and kept under nitrogen until used. The lower molecular weight (*M<sub>n</sub>* of 2170 g/mol) methacrylate-telechelic PTHF (PTHFDMA) macromolecular cross-linker was prepared by reacting hydroxyl-ended poly(tetrahydrofuran) (PTHFDOH) with methacryloyl chloride, while the higher molecular weight (*M<sub>n</sub>* of 6850 and 10000 g/mol) PTHFDMA polymers were synthesized by cationic ring-opening polymerisation of THF followed by in situ methacrylation in our laboratory. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich) was recrystallized from methanol before use. Freshly distilled absolute ethanol and benzene (Spektrum 3D) were used as solvents for the copolymerisation and homopolymerisation, respectively. Methanol (Spectrum 3D) and tetrahydrofuran (Spectrum 3D) were used as received.

### Preparation of PVIIm homopolymer

The PVIIm homopolymer was synthesized by radical polymerisation of *N*-vinylimidazole (VIm) in benzene with AIBN as an initiator. The desired amount of monomer (1.92 mL, 21.2 mmol) was dissolved in benzene, and then the initiator stock solution (18.5 mg, 0.11 mmol) was added to the reaction mixture. Oxygen was removed by a freeze-thaw process. The reaction mixture in a glass reactor tube was kept in an oil bath under nitrogen with constant stirring at 70 °C for a period of 48 h. Then the polymer was dissolved in methanol (30 mL) and precipitated in acetone. The precipitated polymer was filtered and dried first in air and then in vacuum oven at 60 °C. The yield was 67%. The polymer was analyzed by <sup>1</sup>H NMR and Fourier transform infrared spectroscopy.

### Synthesis of PVIIm-*l*-PTHF conetworks

Poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIIm-*l*-PTHF) APCNs were prepared by free radical copolymerisation of *N*-vinylimidazole (VIm) with methacrylate-telechelic PTHF (PTHFDMA) macromolecular cross-linker with different feed compositions (synthesis details and analysis data of PTHFDMA are given in the Supplementary Information). The copolymerisations were carried out in ethanol, a cosolvent for both components in the presence of AIBN initiator at 65 °C, for a period of 3 days. After the successful conetwork syntheses, the solvent was evaporated followed by drying the conetworks under vacuum overnight. The resulting cross-linked polymer conetworks were extracted consecutively with tetrahydrofuran (THF) and then with methanol (MeOH) for one week with both solvents. The amounts of extractables were determined gravimetrically by evaporating the solvents followed by drying the residues to constant weight in vacuum. Finally, the extracted conetworks were dried to constant weight under vacuum at 50 °C. Additional details on the applied materials, the syntheses and analyses of the PTHFDMA macromolecular cross-linkers, PVIIm homopolymers and the PVIIm-*l*-PTHF conetworks are described previously.<sup>15b-d</sup>

### Methods

<sup>1</sup>H NMR spectroscopy was used to obtain the chemical

composition and the purity of the monomers and polymers, both commercial and synthesized, used in this work.  $^1\text{H}$  NMR spectra were obtained on a Varian Unity INOVA spectrometer operating at  $^1\text{H}$  frequency of 400 MHz. Samples were dissolved in appropriate deuterated solvents ( $\text{CDCl}_3$ ,  $\text{D}_2\text{O}$ ). TMS at 0 ppm and  $\text{CDCl}_3$  at 7.28 ppm were used as internal reference for  $^1\text{H}$  NMR.

Solid-state NMR magic angle spinning (MAS) spectra of samples were recorded on the same spectrometer with a Chemagnetics 4.0 mm narrow-bore double resonance T3 probe. The spinning rate of the rotor was 8 kHz in all cases. For the  $^{13}\text{C}$  CP MAS (cross polarization magic angle spinning)<sup>29</sup> spectra 2000-8000 transients were recorded with SPINAL-64 decoupling<sup>30</sup> and 5 seconds of recycle delay. The cross polarization build up curves were recorded in the 0-5 ms contact time range. The measuring temperature was 45 °C (10-30 °C above the melting temperature of PTHF), and the samples were incubated for 2 hours before the measurements. Adamantane was used as external chemical shift reference (38.55 and 29.50 ppm). The 90° pulse lengths were 3.5  $\mu\text{s}$  for carbon and 3.0  $\mu\text{s}$  for the proton channel.

Gel permeation chromatography (GPC) measurements were made with an instrument composed of a Waters 515HPLC pump and Polymer Laboratories Mixed C type column set with three columns. Freshly distilled THF was used as eluent with 1.0 mL/min elution rate, and the detection was carried out by a dual RI and viscosity detector (Viscotek Dual 200). Molecular weight averages and molecular weight distribution (MWD) were calculated by the use of universal calibration made with narrow MWD polystyrene standards in the range of 104 to  $3 \times 10^6$  g/mol.

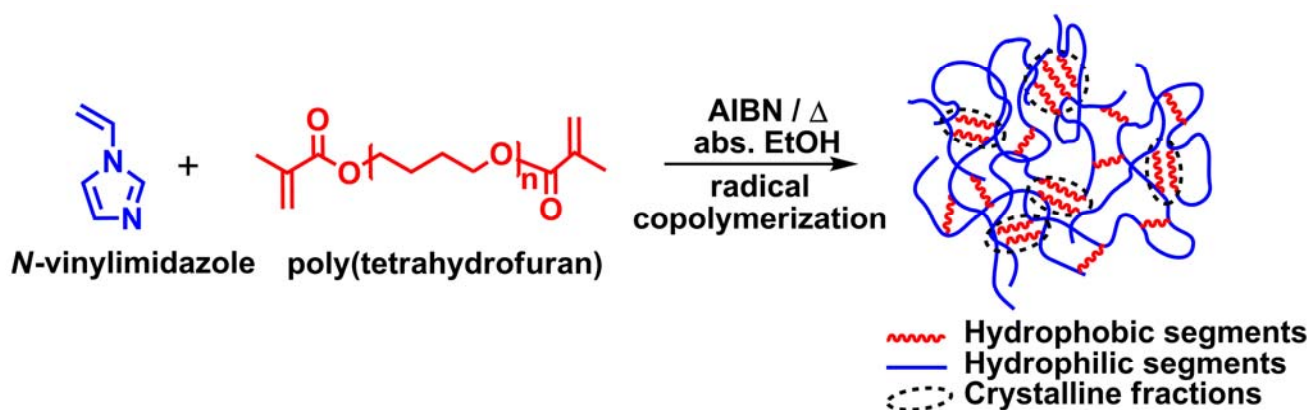
The composition of the conetworks was determined by elemental analysis with a Heraeus CHN-O-RAPID instrument. The chemical compositions were calculated from the atomic

percentages of carbon, nitrogen and hydrogen.

The differential scanning calorimetric (DSC) measurements were made on a Mettler TG50 instrument in a dry nitrogen atmosphere. The APCN samples were annealed (heat treated) to eliminate the effect of thermal history under nitrogen. Samples of about 10-20 mg were used for the DSC measurements. All samples were first heated to 200 °C from -120 °C at a rate of 10 °C/min (first heating scan). Subsequently, the samples were cooled at a rate of 10 °C/min (cooling scan) to -120 °C. Following the cooling scan, the samples were second heated to 200 °C from -120 °C at the same heating rate as in the first scan. The inflection point of the specific heat increase in the transition region during the second heating is reported as the glass transition temperature ( $T_g$ ). The melting temperature ( $T_m$ ) was taken as the minimum of the endothermic peak.

## Results and Discussion

Poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks<sup>15</sup> were prepared by radical copolymerisation of hydrophilic VIm and hydrophobic PTHFDMA macromolecular cross-linkers of various molecular weights as shown in Scheme 1. Successful conetwork syntheses were confirmed by relatively low amounts of extractables in the range of 4-24.5%. As the data indicate in Table 1, three series of conetworks, denoted as V2k, V7k and V10k for conetworks containing PTHFDMA with  $M_n$  of 2170, 6850 and 10000 g/mol, respectively, were obtained in a broad composition range, i. e. with 25-91 wt% PTHF content. (The additional number in sample identification stands for the PTHF content in wt%, i. e. V2k-59 denotes a PVIm-*l*-PTHF sample with 59 wt% PTHF of  $M_n = 2170$  g/mol).



**Scheme 1** Synthesis of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks. The hydrophobic PTHF chains are depicted as the cross-linkers.

**Table 1** Compositions,  $M_c$  values, melting points, crystalline fractions ( $X_c$ ) and glass transition temperatures ( $T_g$ ) of PVIm-*l*-PTHF conetworks with varying molecular weights of methacrylate-telechelic PTHFDMA macromolecular cross-linkers (see Result and Discussion for sample identification).

Sample code	PVIm/PTHF in conetwork (wt %)	$M_c$ of PVIm	$T_m$ (°C)	$X_c$ (%)	$T_g$ (PTHF) (°C)	$T_g$ (PVIm) (°C)
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V2k-25	75/25	3260	--	0	-90	165
V2k-38	62/38	1770	--	0	-81	167
V2k-47	53/47	1220	7	4.5	-80	150
V2k-59	41/59	750	11	9.1	-78	135
V2k-74	26/74	380	14	11.4	-77	127
V2k-89	11/89	130	17	15.2	-76	--
V7k-52	48/52	3120	16	26.3	-85	162
V7k-61	39/61	2160	21	33.9	-82	158
V7k-69	31/69	1520	20	36.7	-76	136
V7k-80	20/80	850	23	36.7	-76	138
V7k-81	19/81	790	23	37.2	-75	140
V7k-84	16/84	650	25	39.1	-74	146
V10k-46	54/46	5790	19	31.3	-91	172
V10k-61	39/61	3150	25	32.6	-89	162
V10k-62	34/66	3020	27	39.8	-86	158
V10k-77	23/77	1470	29	40.0	-82	159
V10k-86	14/86	800	30	41.2	-81	143
V10k-91	9/91	490	30	44.0	-81	141
PVIm	--	--	--	--	--	171
PTHFDMA2k	--	--	25	49.9	-87	--
PTHFDMA7k	--	--	28	60.4	-89	--
PTHFDMA10k	--	--	30	75.4	-89	--

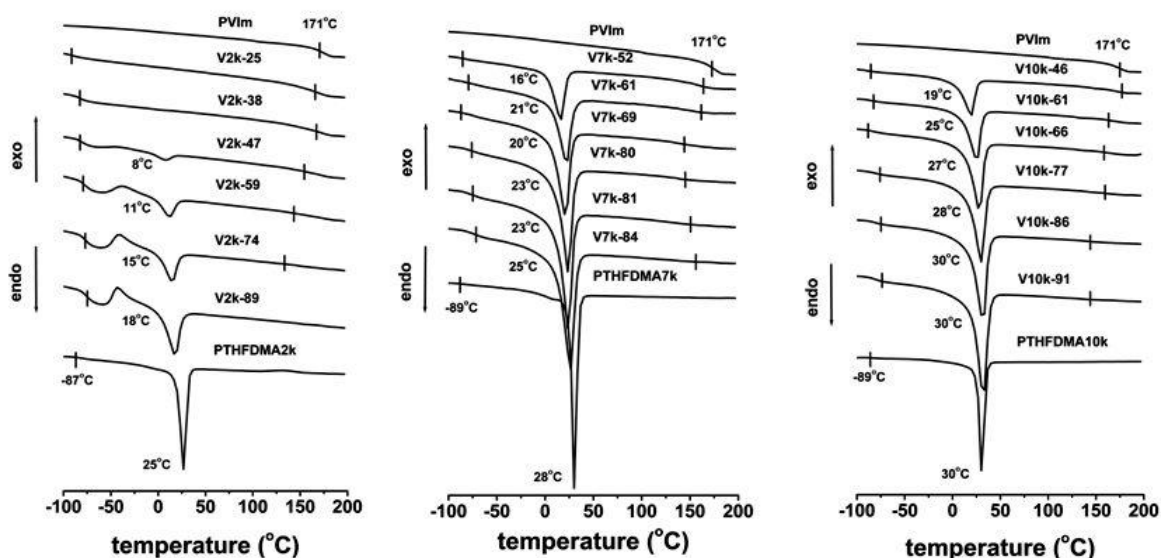
As our attempts to make compatible blends of PVIm and PTHF indicate, these polymers are incompatible (see Table S2 and Figures S26-S29 in the Supplementary Information). Thus, phase separation is expected in the transparent PVIm-*l*-PTHF conetworks, on the one hand. On the other hand, as known, the PTHF homopolymer is a semicrystalline polymer, and its crystallinity is of paramount importance also in determining various properties of the novel PVIm-*l*-PTHF conetworks. Thus, not only amorphous but crystalline regions of PTHF are also displayed in Scheme 1. DSC analyses were carried out in order to reveal the effect of composition and molecular weight of the PTHF macromolecular cross-linker on the phase behavior of the components and crystallinity of PTHF in the PVIm-*l*-PTHF conetworks. Figure 1 shows the DSC thermograms of annealed conetwork samples and the pure components, PTHF and PVIm homopolymers in the -100 to 200 °C region. This temperature range covers the glass transition temperatures of both components and the melting of the semicrystalline PTHF. The PTHF and PVIm homopolymers have glass transition temperature ( $T_g$ ) at -89 °C and 171 °C, respectively.

As displayed in Figure 1, the PVIm-*l*-PTHF conetworks, with the exception of the V2k-25 and V2k-38 samples, show a sharp melting peak in the DSC curves with minima (melting point,  $T_m$ ) in the range of 8-30 °C depending on the MW of the PTHF macromolecular cross-linker and the composition of the conetworks. As also shown in this Figure and Table 1, the  $T_m$  values of PTHF in the conetworks are always lower than that of the corresponding homopolymer, i.e. 25, 28, 30 °C for PTHF with  $M_n$  of 2170, 6850, 10000, respectively. For better visibility, Figure 2, as an example, shows a magnified DSC thermogram of the V7k-52 PVIm-*l*-PTHF sample. This Figure clearly indicates the distinct melting peak of PTHF with  $T_m$  of 16 °C and two glass

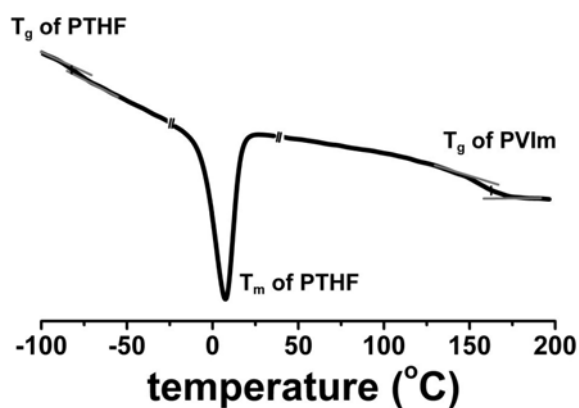
transitions, one at -86 °C for the PTHF and another at 165 °C for the PVIm components. (The larger detailed views of the DSC curves for every sample are shown in Figures S1-S22 in the Supplementary Information.)

As shown in Figure 1, with the exception of sample V2k-89, two distinct glass transition temperatures ( $T_g$ ) are obtained for all the APCN samples. For the V2k-89 sample, the PVIm content is too low for observing its  $T_g$ . These findings indicate phase separation between the covalently cross-linked hydrophilic and hydrophobic components, and partially crystalline PTHF in the PVIm-*l*-PTHF conetworks. Because all the samples are transparent and macroscopically homogeneous, both the separate phases and the crystalline fractions of PTHF in the conetworks form microdomains. Our recent findings by solid state NMR investigations<sup>15d</sup> on dry and swollen PVIm-*l*-PTHF conetworks also corroborate the complete immiscibility of the components in these conetworks.

The  $T_g$  values of PVIm and PTHF in the PVIm-*l*-PTHF conetworks are plotted as a function of the PTHF content in Figure 3. As the data in this Figure and in Table 1 clearly show, the  $T_g$  of PVIm decreases while the  $T_g$  of PTHF increases in the conetworks with increasing PTHF content. The glass transition temperatures of the PVIm phase significantly decrease, up to even by ~30-40 °C, in the conetworks with decreasing PVIm content.



**Fig. 1** Differential scanning calorimetry (DSC) thermograms (second heating scans) of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks and the pure homopolymers (PVIm and PTHF) (heating rate = 10 °C/min; the crossings and the temperature values next to the melting peaks indicate the glass transition and melting temperatures, respectively).



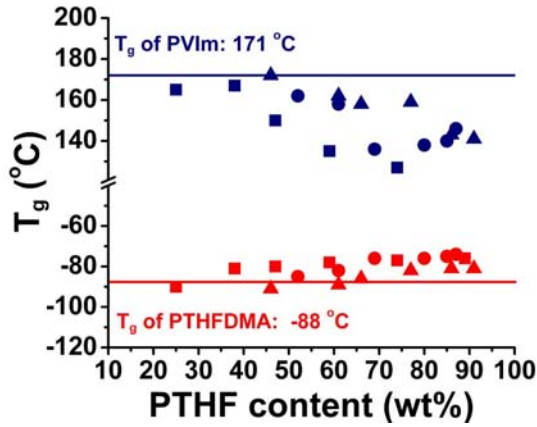
**Fig. 2** Differential scanning calorimetry (DSC) thermogram (second heating scan) of the V7k-52 poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) sample (heating rate = 10 °C/min).

As displayed in Figure 3, there is a monotonous decrease of the  $T_g$  of PVIm with the increase of PTHF content within each conetwork series with a given  $M_n$  of PTHF macromolecular cross-linker, but the extent of  $T_g$  change depends not only on composition, but also on the molecular weight of PTHF. Due to the fact that PVIm and PTHF are not compatible, one can consider that the decrease of the  $T_g$  of the PVIm phase can be

correlated with the average chain lengths, i.e. the average molecular weights ( $M_c$ ) between the cross-linking points. The  $M_c$  of the hydrophilic PVIm segments can be calculated by the following formula:<sup>2a,b,15b-d</sup>

$$M_c = 0.5 \cdot \frac{w_{PVIm}}{w_{PTHF}} \cdot M_{PTHF} \quad (1)$$

where  $w_{PVIm}$ ,  $w_{PTHF}$ , and  $M_{PTHF}$  stand for the weight fraction of PVIm, the weight fraction of PTHF determined by elemental analyses, and the number average molecular weight of the PTHF macromolecular cross-linker, respectively. The  $M_c$  of the PVIm segments covers a broad range, i. e. from 130 to 5790 in the investigated conetworks (from 130 to 3560, from 650 to 3120 and from 490 to 5790 for the V2k, V7k and V10k PVIm-*l*-PTHF conetwork series, respectively).

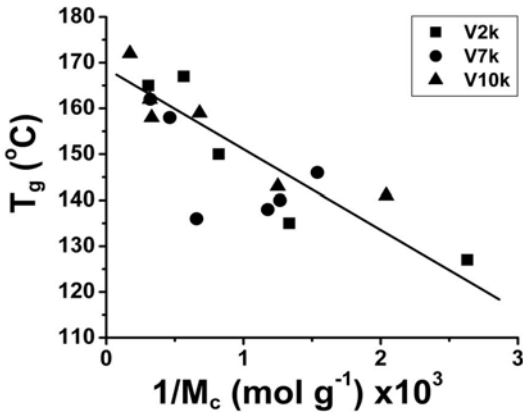


**Fig. 3** Glass transition temperature ( $T_g$ ) values of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks as a function of composition ((■) V2k, (●) V7k, (▲) V10k PVIm-*l*-PTHF series, and the lines represent the  $T_g$  of the PTHFDMA macromolecular cross-linkers and the PVIm homopolymer).

Plotting the  $T_g$  of the PVIm phase as a function of  $1/M_c$  (Figure 4) clearly indicates that the data can unexpectedly be approximated with a straight line, i. e. the tendency of the data shows linear decrease of  $T_g$  with increasing  $1/M_c$ . Surprisingly, this relation is similar to the Fox-Flory equation<sup>31</sup> for homopolymers, according to which the  $T_g$  dependence can be given by the following equation:

$$T_g = T_{g,\infty} - \frac{K}{M_n} \quad (2)$$

where the  $T_{g,\infty}$  is the glass transition temperature of the polymer with infinite molecular weight,  $M_n$  stands for the number average molecular weight of the polymer and  $K$  is a constant.



**Fig. 4** Glass transition temperature ( $T_g$ ) values of poly(*N*-vinylimidazole) as a function of  $1/M_c$  in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks.

By substituting  $M_n$  with  $M_c$  in Equation (2), the Fox-Flory type correlation between  $T_g$  and  $M_c$  for the PVIm component of the conetworks indicates that the macromolecular PTHF cross-linker acts as a “scissor” for the PVIm chains in the PVIm-*l*-PTHF conetworks. In other words, in respect of glass transition of PVIm in the conetworks it seems that the grafted macromolecular PTHF

cross-linkers “cut” the PVIm chains like a scissor. As a consequence, this unprecedented result, that is the linear  $T_g$  versus  $1/M_c$  correlation for PVIm, indicate that the PVIm chains in the conetworks behave from the point of view of glass transition as “free” chains with the determining molecular weight of  $M_c$ . To the best of our knowledge, such scissor effect by the macromolecular cross-linker and the unexpected correlation between  $T_g$  and  $M_c$  have not been described at all for conetworks yet. It has also to be noted that the intercept (169 °C) in the  $T_g$  versus  $1/M_c$  plot results in with good approximation the measured  $T_g$  of the PVIm homopolymer (171 °C) which further supports the scissor effect of the PTHF cross-linkers in the PVIm-*l*-PTHF conetworks.

As recent solid state static deuteron NMR investigation on a similar APCN system indicates,<sup>1m</sup> the mobility and the motion of the cross-linking points differs from the main-chain molecules. Around and above the glass transition temperature of the glassy components, the cross-linker molecules are doing a “crankshaft” motion. This peculiar behavior can also support the scissor effect.

The  $T_g$  change of PTHF with composition in the conetworks, shown in Figures 3 and S23, that is the increase of the  $T_g$  of PTHF with its increasing content, is even more surprising. In the case of partial miscibility, the tendency of  $T_g$  change should be the reverse, i. e. the  $T_g$  of PTHF in the conetworks should increase with decreasing PTHF content.

The mobility on the molecular level (molecular motion) in the PVIm chain and interaction of the chain in the conetworks were investigated by solid state <sup>13</sup>C CP MAS NMR spectroscopy. The build up curves in these measurements were constructed by varying the contact time and plotting peak intensity vs. contact time. The experimental curves were fitted with a simplified expression which enables determination of the changes in the environment and relaxation behavior:

$$M(t) = \lambda^{-1} M_0 \left[ 1 - \exp\left(-\frac{\lambda t}{T_{CH}}\right) \right] \exp\left(-\frac{t}{T_{1\rho H}}\right) \quad (3)$$

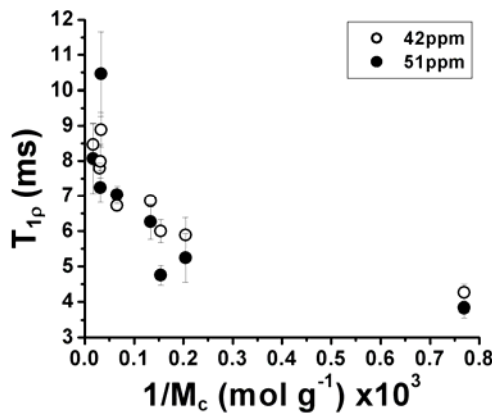
where  $\lambda = 1 + (T_{CH}/T_{1\rho C}) - (T_{CH}/T_{1\rho H})$ ,  $M(t)$  is the magnetization at contact time  $t$ ,  $M_0$  is the initial magnetization,  $T_{CH}$  is the time coefficient of the cross polarization (the time it takes for magnetization to be transferred from <sup>1</sup>H to <sup>13</sup>C), and  $T_{1\rho}$  is the relaxation time in the rotating frame. If  $T_{1\rho}$  relaxation time is much larger than the cross polarization coefficient ( $T_{CH}$ ), Equation (3) can be simplified with the approximation  $\lambda = 1$ . In our case, this simplification can be used also for the main chain signals of the PVIm component. It has to be noted that all the measurements were carried out at 45 °C, that is above the melting point of the PTHF phase in order to avoid any effect by the microcrystalline domains of this polymer in the conetworks.

The  $T_{CH}$  coefficient was found to be the same for all the samples, indicating that there is no change in the environment of main chain carbons depending on the  $M_c$  and composition of the APCNs. The build-up curves of the PTHF signals are increasing in the investigated contact time interval (0-5 ms), no decreasing can be observed. By combining these facts, we can rule out the existence of mixed phases between PVIm and PTHF in the conetworks. However, we have to note the unexpected dependence of the  $T_{1\rho}$  relaxation time as a function of  $1/M_c$ . This



relaxation parameter is very sensitive signal of molecular motion in polymers.<sup>32</sup> Thus, the data shown in Figure 5 can be directly connected to the segment motion on molecular scale of the main PVIm chain. Because the PVIm phase is in glassy state at the measuring temperature (45 °C), the molecular motion in the conetworks can be assigned to the kink motion of the main chain. Surprisingly, the relaxation time depends on the average molecular weight between cross-linking points ( $M_c$ ), and the observed values are lying on a master curve for all the investigated samples containing PTHF macrocross-linker with different molecular weights. The data displayed in Figure 5 also indicate that the molecular motion in the PVIm chains in the conetworks follow similar tendency than that of the glass transition temperatures (Figure 4) as a function of  $1/M_c$ .

As to the crystallisation of PTHF in the PVIm-*l*-PTHF conetworks an interesting phenomenon can be revealed by the detailed analysis of the DSC thermograms in Figure 1. A closer look at the data in Figure 1 and Table 1 allows concluding that both the crystalline fraction and the melting temperatures of PTHF in the PVIm-*l*-PTHF conetworks decrease with decreasing PTHF content. In the case of the V2k conetwork samples, crystalline PTHF cannot be observed for the conetworks with 25 and 38 wt% PTHF content at all, i. e. surprisingly the PVIm phase completely suppresses crystallisation of the PTHF component in these PVIm-*l*-PTHF conetworks. It is interesting to note that Lequieu and Du Prez<sup>11b</sup> reported on the absence of the melting peak of PTHF in a poly(*N*-isopropyl acrylamide)-*l*-poly(tetrahydrofuran) conetwork sample with relatively low PTHF content. Suppression of crystallisation of PTHF was recently also observed by Meyer et al.<sup>33</sup> in the case of PTHF-diacrylate homopolymer networks with low molecular weight ( $M_n = 1050$  and 2500) PTHF precursors. Diminishing of crystallisation of poly(ethyleneglycol) (PEG) was also reported for PEG-polyisobutylene conetworks.<sup>1e</sup>



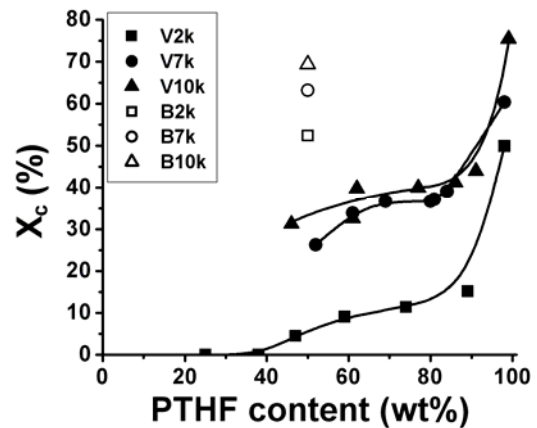
**Fig. 5** Relaxation time ( $T_{1\rho}$ ) of poly(*N*-vinylimidazole) main chain carbons as a function of  $1/M_c$  in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks. The CH and CH<sub>2</sub> groups of the main chain of the PVIm component have chemical shifts at 51 and 42 ppm, respectively.

By determining the area under the melting peak in the DSC curves, the extent of crystallisation ( $X_c$ ) in the conetworks can be obtained. Thus the  $X_c$  of the PTHF phase is calculated as the ratio of the heat of fusion of the normalized PTHF content in the

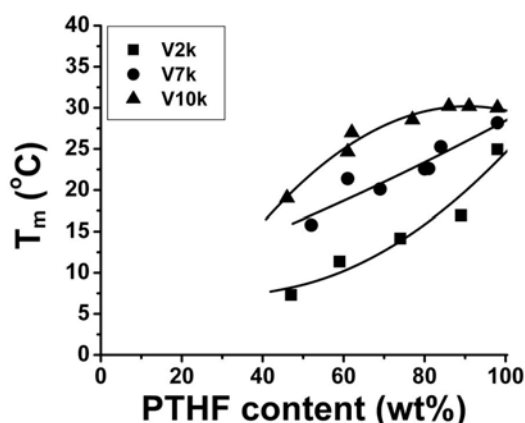
PVIm-*l*-PTHF conetworks ( $\Delta H_{\text{exp}}$ ) relative to that of the pure semicrystalline PTHF macromolecular cross-linker ( $\Delta H_{\text{PTHF}} = 167$  J/g enthalpy of melting<sup>28b</sup>) according to the following equation:

$$X_c = \frac{\Delta H_{\text{exp}}}{\Delta H_{\text{PTHF}}} \quad (4)$$

where  $\Delta H_{\text{exp}}$  is normalized to the PTHF weight fraction in the conetworks. Figure 6 shows the extent of crystallisation as a function of PTHF content in the PVIm-*l*-PTHF conetworks. Surprisingly, evaluation of the melting data shows that the crystallisation and thus the crystalline fraction of PTHF are significantly suppressed by even a minimal content of the glassy PVIm (~10 %) in these materials. The crystallisation of PTHF drastically decreases in the case of the V2K-89 APCN from 49.9% to 15.2% only with 11 wt% PVIm in the conetwork. The samples with higher molecular weight cross-linkers show the same trend. The highest molecular weight PTHF (10k) homopolymer has a crystallinity of 75.4%, which decreases to 44% with the impact of only 9 wt% PVIm. Figure 6 also shows that the longer, higher molecular weight PTHF cross-linkers in the conetworks are more capable of crystallisation, than the shorter, lower molecular weight cross-linkers. This means that the crystalline fraction of PTHF in the PVIm-*l*-PTHF conetworks depends not only on the composition but also on the molecular weight of the macromolecular PTHF cross-linker.



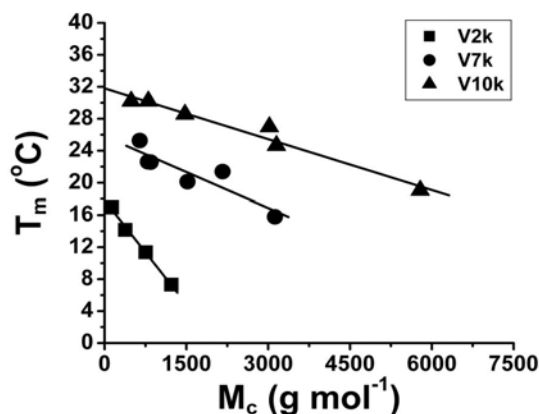
**Fig. 6** Crystalline fraction ( $X_c$ ) of poly(tetrahydrofuran) as a function of the relative amount of PTHF in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks and in the blends of PTHF and PVIm homopolymers with 50:50 wt% polymer ratios (B2k, B7k and B10k; open symbols).



**Fig. 7** Melting point ( $T_m$ ) of poly(tetrahydrofuran) as a function of the relative amount of PTHF in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIIm-*l*-PTHF) conetworks.

It should be noted that in the case of blends of PTHF and PVIIm homopolymers (50:50 wt% PVIIm/PTHF) there are no significant changes in the crystalline fraction compared to the pure PTHF macromolecular cross-linkers, i. e. the glassy PVIIm has no effect on PTHF crystallisation in these homopolymer mixtures (Figure 6). This also indicates the incompatibility of the PTHF and PVIIm homopolymers. (The DSC curves for every blend are shown in Figures S25-S29 and the data are summarized in TableS1 in the Supplementary Information.)

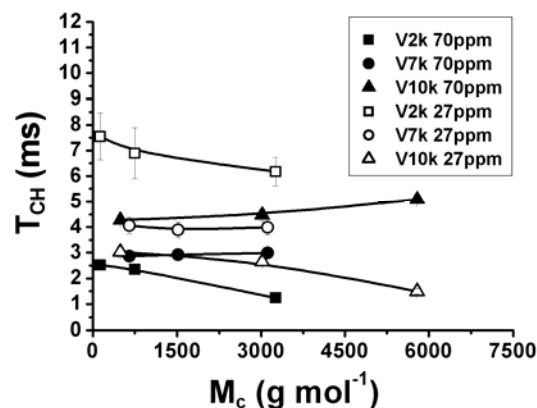
Figure 7 reveals that both the composition and the length of the PTHF cross-linker have effect on the melting temperature of the semicrystalline hydrophobic PTHF component in the PVIIm-*l*-PTHF conetworks. According to this Figure, the  $T_m$  values of PTHF in the conetworks increase with increasing PTHF content in the conetworks and also with the molecular weight of the macromolecular PTHF cross-linkers.



**Fig. 8** Melting point ( $T_m$ ) of poly(tetrahydrofuran) as a function of the average molecular weights of the hydrophilic PVIIm segments between two cross-linking points ( $M_c$ ) in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIIm-*l*-PTHF) conetworks.

There are several structural parameters in the polymer conetworks, such as the average molecular weights of the hydrophilic PVIIm segments between two cross-linking points ( $M_c$ ), the composition of the conetworks and the number average molecular weight of the hydrophobic macromolecular cross-

linker. Figure 8 shows the  $T_m$  data as a function of the  $M_c$  of the PVIIm component in the conetworks. As shown in this Figure, the melting temperatures of the PTHF component are unpredictably linearly decreasing with  $M_c$  within each conetwork series with fixed  $M_n$  of the PTHF cross-linker. This unexpected correlation between  $T_m$  and  $M_c$  of PVIIm indicates that the length of the surrounding PVIIm chains interrupted with PTHF cross-linker play a crucial role in the determination of  $T_m$  of PTHF in the PVIIm matrix.



**Fig. 9** Time coefficient of the cross polarization ( $T_{CH}$ ) of the poly(tetrahydrofuran) phase as a function of the average molecular weights of the hydrophilic PVIIm segments between two cross-linking points ( $M_c$ ) in the poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIIm-*l*-PTHF) conetworks. The  $\text{CH}_2\text{-O}$  and  $\text{CH}_2$  groups of the PTHF component have chemical shifts at 70 and 27 ppm, respectively.

The above discussed unexpected phenomenon is well reflected by the dependence of the  $T_{CH}$  coefficient of the PTHF component on  $M_c$ . While this coefficient is constant for the PVIIm phase for all the samples, it shows a dependence not only on the chain length of PTHF but also on the  $M_c$  of PVIIm as displayed in Figure 9. However, although the PTHF phase is in molten state and no mixed phase can be observed, the magnetization transfer from H to C shows a surprising dependence. The cause of this phenomenon should be exclusively found in the PTHF phase. The magnetization transfer can occur not only between the directly connected CH pairs, but also between the neighboring  $\text{CH}_2$  groups, and even between adjacent chains. Changes of the  $T_{CH}$  parameter alludes to change in the CH distances, which can be originated from varying the PTHF chain conformation and/or density of the polymer chains. This unpredicted behavior of the PTHF phase, that is the dependence of  $T_m$  and  $T_{CH}$  on structural parameters, makes questionable conventional description of these complex structures, which postulates the independence of separated phases.

## Conclusion

A series of novel poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIIm-*l*-PTHF) amphiphilic conetworks were successfully synthesized in broad composition ranges by free radical copolymerisation of hydrophilic VIm with hydrophobic methacrylate-telechelic PTHF macromolecular cross-linker of varying molecular weights in a common solvent for both components. The systematic thermal analysis of these novel



materials revealed that the transparent conetworks possess two distinct glass transition temperatures ( $T_g$ ) corresponding to the  $T_g$ s of the respective homopolymer components. This phenomenon allows to confirm the existence of microphase separation in these conetworks. Immiscibility of the pure PVIm and PTHF homopolymers and the results of solid state NMR investigations this and a previous study<sup>15d</sup> also corroborate the complete phase separation in the PVIm-*l*-PTHF conetworks. These findings are in good agreement with the results of solid state NMR spin diffusion<sup>3c</sup> investigations on poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene conetworks, according to which separated nanophases with sharp interfacial boundaries, that is without mixed interface, exist in these conetworks. Surprisingly, Fox-Flory type correlation was found between the  $M_c$  (average molecular weight between cross-links) of the PVIm component and its glass transition temperatures indicating that the macromolecular PTHF cross-linker acts as a “scissor” in these novel materials, i. e. the glass transition of the PVIm chain segments is determined by their segment lengths between two cross-linking points and not by its full length in the conetworks. According to our knowledge, theoretical prediction does not exist for describing such a phenomenon and  $T_g$  versus  $M_c$  correlation in two-component cross-linked macromolecular assemblies. Interestingly, similar trend was found between the  $T_{1\rho}$  relaxation time, i. e. molecular mobility of PVIm, and  $M_c$  by solid state NMR measurements.

It was also found that the melting temperature ( $T_m$ ) and the crystalline fraction ( $X_c$ ) of the PTHF phase is suppressed by even the minimal content of PVIm in the conetworks. The obtained data indicate that both the decrease of  $T_m$  and  $X_c$  of PTHF is not only composition dependent, but the molecular weight of the macromolecular PTHF cross-linker and unexpectedly the  $M_c$  of the PVIm component as well have effect on these morphological parameters. In conetworks with constant  $M_n$  of the PTHF cross-linker, the  $T_m$  of PTHF linearly decreases with the  $M_c$  of PVIm. The relationship of the  $T_{CH}$  coefficient of PTHF, measured by solid state NMR, with  $M_c$  is in line with these observation.

These unprecedented new findings, not predicted by any existing theoretical considerations for bicomponent polymer systems, on the correlation between the basic structural parameters, such as composition,  $M_c$  and molecular weight (MW) of the macromolecular cross-linker, and the fundamental thermal properties ( $T_g$ ,  $T_m$  and  $X_c$ ) of the novel PVIm-*l*-PTHF conetworks affords to control these material characteristics by selecting the proper synthetic parameters, i. e. composition of the feed and MW of the telechelic macromolecular cross-linker. On the other hand, our results also indicate that covalently bonding different polymer chains in conetworks may lead to a variety of new materials with properties not accomplished so far.

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