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Poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) amphiphilic conetworks and gels: molecularly forced blends of incompatible polymers with single glass transition temperatures of unusual dependence on composition

Csaba Fodor,[a*†] Tímea Stumphauser,[a] Ralf Thomann,[b] Yi Thomann,[b] and Béla Iván[a*]

A series of macroscopically homogeneous poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) ("*l*" stands for "*linked by*") amphiphilic conetworks (APCNs) composed of otherwise incompatible polymers were successfully synthesized in a broad composition range (34-88 wt% PPG) by free radical copolymerization of hydrophilic *N*-vinylimidazole (VIm) and hydrophobic poly(propylene glycol) dimethacrylate (PPGDMA) macromolecular cross-linker. Strikingly, while PVIm and PPGDMA homopolymers are immiscible and their blends have two distinct glass transition temperatures (T_g), the PVIm-*l*-PPG conetworks possess only one T_g indicating the absence of considerable phase separation in the conetworks, which was also confirmed by AFM measurements. This is in sharp contrast to the two T_gs of APCNs reported so far in the literature, on the one hand. On the other hand, the T_g values do not follow known correlations between T_g and composition, like the Fox equation or additive rule, widely applied for compatible polymers. These results indicate strong interpolymer interaction on molecular level between the PVIm and PPG chains in these new APCNs resulting in single T_g. Thermogravimetric analysis (TGA) shows that degradation of the conetworks occurrs at high temperatures in two stages without sharp changes, but with a transition period in between. The DTG curves indicate that the components keep their chemical integrity to certain extent in these APCNs. The amphiphilic nature of the PVIm-*l*-PPG conetworks was confirmed by their composition dependent swelling in both polar (water, ethanol) and nonpolar (THF) solvents, that is, in spite of the lack of phase separation, these new materials behave as either hydrogels or hydrophobic gels (organogels) depending on the swelling medium in a broad composition range.

Introduction

Bi- or multicomponent three-dimensional polymer networks of covalently bonded hydrophilic and hydrophobic polymer chains, in particular amphiphilic conetworks (APCNs)[1-12] belong to a special class of rapidly emerging nanostructured cross-linked macromolecular materials. Due to the coexistence of chemically bonded, otherwise immiscible, hydrophilic and hydrophobic (or even hydrophilic/fluorophilic and hydrophobic/fluorophilic[3]), macromolecules in one cross-linked structure, APCNs have a variety of unique physical and chemical properties. These materials possess unique swelling ability,[4] i. e. they behave either as hydrogels or hydrophobic gels (organogels) depending on the solvent, as well as anomalous swelling behavior,[5] improved mechanical characteristics compared to homopolymer hydrogels,[6] and excellent biocompatibility or biostability.[7] Moreover, these soft materials possess bicontinuous (cocontinuous) nanophasic morphology in broad composition ranges as it has been shown by a variety of techniques, such as transmission electron microscopy (TEM),[8] atomic force microscopy (AFM),[8a-c,9] small angle X-ray scattering (SAXS),[2b,8a,d,10] small angle neutron scattering (SANS),[11] and solid-state NMR.[10,12] As a consequence of these properties, APCNs have attracted significant attention in both material science and biomedical application fields in recent years. (see e. g., refs. 4-14 and references therein). Therefore, it is a challenging task to investigate the synthesis possibilities, structure and properties of unexplored new combinations of immiscible hydrophilic and hydrophobic polymeric components as building blocks of APCNs by forcing them into conetwork assemblies. So far, the large majority of conetworks have been obtained by copolymerizing telechelic macromonomers as polymeric cross-

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Electronic Supplementary Information (ESI) available: ^{1}H NMR and GPC of poly(propylene glycol) dimethacrylate (PPGDMA) macromolecular cross-linker, feed ratios and amounts, pictures and DSC results of poly(*N*-vinylimidazole) and poly(propylene glycol) (PVIm-*blend*-PPG) mixtures, AFM, TEM, TGA, DTG results, and water adsorption measurements of PVIm-*l*-PPG conetworks. See DOI: 10.1039/x0xx00000xFootnotes relating to the title and/or authors should appear here.

linkers with low molecular weight monomers (this is called the macromonomer technique).[1-12] Telechelic macromonomers utilized until now for this purpose have been exclusively obtained as laboratory products with average molecular weights over 1000 g mol^{-1}. Our attention has recently turned to a commercially available telechelic macromonomer, poly(propylene glycol) dimethacrylate (PPGDMA) having lower than 1 kD average molecular weight as a hydrophobic component of amphiphilic conetworks. For the hydrophilic constituent, poly(*N*-vinylimidazole) (PVIm) has been selected due its exceptional chemical and physical properties, in order to obtain and investigate poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) (“*l*” stands for “*linked by*”) amphiphilic conetworks which have not been explored according to the best of our knowledge so far.

The interest in PVIm, in addition to its valuable commercial applications, arises also from the fact that imidazole, the heterocyclic aromatic side group of PVIm, is one of the most important heterocyclic aromatic moiety in biological systems. Imidazole and its derivatives are present in all the important biomacromolecules, such as proteins (histidine), nucleic acids (purine ring of adenine and guanine) and hormones (histamine). Moreover, as functional group it is also a building block of metalloproteins (hemoglobin, carbonate dehydratases, carboxypeptidase A), B12 vitamin, their derivatives and a variety of pharmaceutical compounds and pesticides etc. Recently, PVIm has received great attention not only as components in APCNs,[5,12c,13] but due to its polyelectrolyte property and to the dual character of the polymer, the hydrophobic main chain and the hydrophilic imidazole ring, in various areas of promising new material systems. Moreover, polymers with imidazole moieties have been investigated in diverse application fields, such as in fuel cells,[14] ion imprinted matrices,[15] metal ion complexing membranes,[16] electrophoresis medium,[17] gene delivery vectors,[18] enzyme immobilization carrier,[19] catalysts and catalyst supports[20] and polyionic liquids[21] etc. In our previous publications, the synthesis and unprecedented structure-property correlations of PVIm based conetworks linked by poly(tetrahydrofuran) (PTHF) dimethacrylate having molar mass higher than 2000 g mol^{-1}, with phase separated morphology were reported.[5,12c,13]. As an alternative, the commercially available PPGDMA with relatively low molecular weight and different hydrophobicity than PTHF caught our attention for macromolecular cross-linker in PVIm-based APCNs. Although PPG has several advantageous properties and a variety of PPG containing macromolecular structures, based mainly on PPG macromonomers, have been investigated in recent years,[22] only one example of APCN with PPG component, combined with poly(2-hydroxyethyl methacrylate) (HEMA), has been reported in the literature so far.[23] In these publications, Matsumoto *et al.* described the free radical copolymerization behaviour of PPGDMA and HEMA, and investigated the swelling behaviour of the resulting conetwork in mixed solvents.

On the basis of the considerations outlined above, the aim of the present work is to incorporate the hydrophilic PVIm and hydrophobic PPG into a single macromolecular assembly by synthesizing PVIm-*l*-PPG APCNs and investigate the fundamental properties of the resulting conetworks. Cross-linked macromolecular structures consisting of these polymers, especially with a relatively low molecular weight macromolecular cross-linker, such as the commercially available telechelic PPGDMA, is of interest not only because of the lack of reports on PVIm-*l*-PPG conetworks but also because of the lack of systematic investigations on the synthesis and characterization of amphiphilic conetworks with macromolecular cross-linkers having less than 1000 molecular weight in general. Thus, the suitable reaction conditions of the network forming free radical copolymerization of hydrophilic VIm with the hydrophobic PPGDMA as macromolecular cross-linker, and the unique effect of composition on glass transition indicating unprecedented miscibility of the incompatible components in the conetwork structure, the thermal decomposition and swelling behaviour of the resulting new cross-linked materials are reported herein.

Experimental

Materials. *N*-vinylimidazole (VIm, Aldrich) was vacuum distilled from CaH_2 (95%, Aldrich) at 72 ^{o}C, and kept under nitrogen until used. Poly(propylene glycol) dimethacrylate (PPGDMA) (M_n = 560) were purchased from Aldrich and was purified using Al_2O_3/silica gel and inhibitor-remover (Aldrich) and stored at 5 ^{o}C before use. 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 copolymerization and homopolymerization, respectively. Tetrahydrofuran (min. 99%, Spectrum 3D) was used as received for the swelling experiments. Distilled and deionized water was used in experiments carried out with water.

Synthetic procedures

Preparation of poly(*N*-vinylimidazole) (PVIm) homopolymer. The PVIm homopolymer as control material for the thermal measurements was synthesized by radical polymerization of *N*-vinylimidazole (VIm) in benzene with AIBN as an initiator as it was described by us previously.[12c] The purified PVIm was characterized by viscosity average molecular weight measurement (M_v = 126800 g mol^{-1}).

Preparation of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks. The PPGDMA macromolecular cross-linker was purified from the inhibitors by passing through a column filled with Al_2O_3/silica gel and inhibitor-remover. The purified PPGDMA was characterized by GPC (M_n = 1000 g mol^{-1}, M_w = 1020 g mol^{-1}, M_w/M_n = 1.02) and by ^1H NMR measurements (M_n = 560 g mol^{-1}, F_n = 2.0) (the ^1H NMR spectrum and GPC chromatograms are displayed in Figure S1 in the Electronic Supplementary Information). The PVIm-*l*-PPG APCN samples were prepared by free radical copolymerization of VIm comonomer and PPGDMA as macromolecular cross-linker with AIBN as initiator. In brief, for the synthesis of the conetworks, the desired amount of the PPGDMA cross-linking agent and VIm comonomer, initiator stock solution and ethanol, common solvent for all the components, were measured in glass vials. The reaction mixtures were homogenized and by nitrogen purging the oxygen was removed. The solutions were poured into teflon molds in an AtmosBag™ (Sigma Aldrich) under nitrogen atmosphere. Then the molds were closed under nitrogen and kept in an oven at 65 °C for a period of 72 hours. Subsequently, the molds were cooled to room temperature, the solvent was evaporated and the conetworks were dried under vacuum. The resulting cross-linked polymers were extracted with ethanol (EtOH) for one week. Finally, the extracted conetworks were dried to constant weight under vacuum at 50 °C.

Preparation of poly(*N*-vinylimidazole) and poly(propylene glycol) (PVIm-*blend*-PPG) homopolymer blends. For the preparation of blends of PVIm and PPG homopolymers, both polymers were dissolved in the EtOH cosolvent separately. Then, the solutions were mixed to obtain mixtures with different PVIm/PPG weight ratios (20:80, 40:60, 60:40 and 80:20) with moderate shaking for few hours at room temperature. The prepared mixtures were poured into a glass mould and the solvent was removed by slow evaporation. Thin films were formed, which were finally dried under vacuum to constant weight to remove the residual solvent.

Annealing of the poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks. Heat treatment was carried out with the dried PVIm-*l*-PPG conetworks with thickness of c.a. 2-3 mm. The samples were annealed under nitrogen atmosphere at high temperature (200 °C) in a vacuum oven for 5 h. The temperature was increased stepwise, and the samples were let slowly cool down under nitrogen atmosphere after the heat treatment. The annealed conetworks were investigated by differential scanning calorimetry (DSC) and atomic force microscopy (AFM) measurements.

Instruments and measurements

The chemical composition and the purity of the compounds were determined by Nuclear Magnetic Resonance (NMR) measurements on a Mercury Plus Varian VRX-200 (^{1}H: 200 MHz; ^{13}C: 50.31 MHz) spectrometer at room temperature. Chemical shifts (δ) are reported in ppm and the spectra were referenced to the solvent residual peaks ($CDCl_3$ at 7.28 ppm and DHO at 4.79 ppm).

Gel permeation chromatography (GPC) measurements were made with an instrument composed of a Waters 515 HPLC pump and Polymer Laboratories Mixed C type column set with three columns. Freshly distilled THF was used as eluent with 1.0 mL min^{-1} 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 $3{\cdot}10^6$ g mol^{-1}.

Viscosity average molecular weight measurement was performed by using Ubbelohde capillary type viscometer. The Mv value was calculated from the Mark-Houwink-Sakurada equation, $[\eta] = K{\cdot}M^{\alpha}$, where $K = 1.22{\cdot}10^{-3}$ mL g^{-1} and $\alpha = 0.51$ in aqueous 0.1 M NaCl solution at 25°C.[24]

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 and thermogravimetric analysis (TGA) were made on a Mettler TG50 instrument under dry nitrogen atmosphere. The APCN samples were annealed (heat treated) to eliminate the effect of thermal history under nitrogen. The heating rate was 10 °C min^{-1} under nitrogen atmosphere. 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 decomposition temperature ($T_{d(max)}$) of the polymers was assigned to the temperature of the maximum rate of weight loss. Programmed heating cycles from -120 °C to 200 °C and from 35 °C to 750 °C were used for DSC and TGA analysis, respectively.

Atomic force microscopy (AFM) experiment was performed on a MultiMode scanning probe microscope with Nanoscope IIIa controller (Digital Instruments) at ambient condition in height and phase imaging modes. The flat cryo-sectioned surface of the annealed conetwork used for examination was obtained by using a Diatome diamond knife at -100 °C using a Leica EMFCS microtome.

Transmission electron microscopy (TEM) experiments were performed on a Zeiss LEO 912 Omega microscope with an acceleration voltage of 120 KV. Like sectioning surfaces for AFM, sections were obtained for TEM and stained with OsO_4 for 20 minutes.

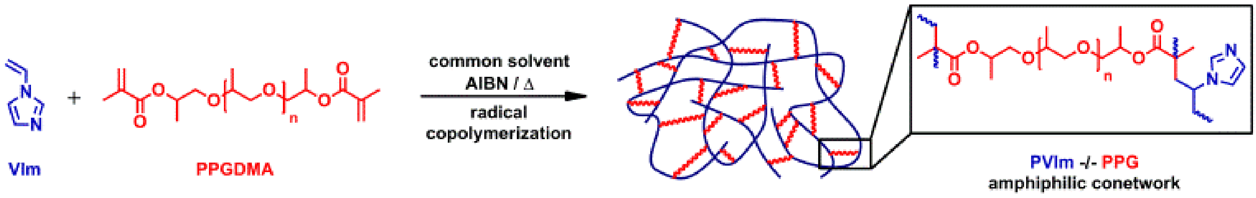
The solvent uptake ratios of the conetworks were determined gravimetrically in nonpolar (THF) and polar (water) solvents. Dried polymer samples were used and placed in the selected solvent at room temperature and were left to swell until constant weight. The samples were removed from the solvent between-times, wiped with a filter paper and weighed, and placed back in the solvent bath until the equilibrium swelling ratios (Q) were obtained at constant weight, calculated by the following relation:

$$Q = \frac{m - m_0}{m_0}$$

where m and m_0 are the weights of the swollen and the dry conetworks, respectively.

Results and discussion

Synthesis of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks. The radical copolymerization of VIm and PPGDMA was carried out by using various feed ratios in ethanol, a cosolvent for all the components (VIm, PVIm and PPGDMA) at 65 °C with AIBN as initiator under nitrogen atmosphere as shown in Scheme 1.



Scheme 1. The formation of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetwork by radical copolymerization of *N*-vinylimidazole (VIm) with telechelic poly(propylene glycol) dimethacrylate (PPGDMA) macromonomer.

As depicted in this Scheme, this process results in a cross-linked structure in which the PVIm chains are connected with the PPGDMA bismacromonomer.After successful copolymerizations, all the resulting materials were extracted with ethanol, a common solvent for all the components in order to remove the unreacted monomer, macromonomer, homopolymer and partially polymerized macromolecular cross-linker. As shown in Table 1, reasonably low amounts of extractables, i. e. 3-15 wt%, were obtained, which indicate successful conetwork formation by applying the investigated broad range of feed ratios. In all cases, macroscopically homogeneous and transparent materials were obtained. The fundamental structural parameters of the resulting conetworks are the average molecular weights of the hydrophilic and hydrophobic components, the approximated cross-link density and the overall gel composition. The segment length of the used PPGDMA cross-linker is given in our case, while the average molecular weights of the hydrophilic PVIm segments between two cross-linking points (Mc) in the conetworks were calculated by the following formula, which does not consider loops or loose chains in the structure:[4(a,b),5,13c]

$$M_c = 0.5\frac{w_{PVIm}}{w_{PPG}}M_{PPGDMA}$$

where w_{PVIm}, w_{PPG}, and M_{PPGDMA} stands for the weight fractions of PVIm, PPG, and the number average molecular weight of the PPGDMA macromer, respectively.

Table 1 shows the VIm/PPGDMA feed ratios, the composition of the conetworks determined by elemental analysis after extraction, and the average molecular weight of the hydrophilic PVIm segments between cross-linking points. The number in the sample identification in this Table and rest of this study stands for the PPG content in the conetworks determined by elemental analysis. As shown in Table 1, two series of conetworks (P1 and P2) with 20-70 wt% PPG feed ratios were prepared independently, and comparison of the compositions indicates good reproducibility of the conetwork synthesis. The applied conditions resulted in PVIm-*l*-PPG conetworks with a broad composition range, i. e. with 34-88 wt% PPG content. The low M_c values for conetworks with relatively high PPG cross-linker contents indicate that the macromonomers are coupled not only to the VIm monomer units but to each other as well in these PVIm-*l*-PPG samples.

As the data indicate in Table 1, the PPG content is higher in the conetworks than in the corresponding feeds, and it ranges between 34 and 88 wt%. The correlation between the feed ratios and the compositions of the final (extracted) PVIm-*l*-PPG conetworks are shown in Figure 1. This Figure displays the relative amounts of PPG in the conetworks as a function of the PPG content in the feed. It is evident from these data that the applied synthesis process provides very good reproducibility. It can also be seen that there is a significant deviation between the feed ratios and the composition of the formed PVIm-*l*-PPG APCNs, as also shown in Table 1.

Table 1. Feed ratios, composition, extractables and average molecular weights of PVIm between cross-links (M_c) in the poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks.

Sample ID	Composition (PVIm/PPG) in feed (wt%)	Composition (PVIm/PPG) in conteworks (wt%)	Extractables	M_c(PVIm) (g·mol^{-1})
P1-34	80/20	66/34	8.3	544
P1-52	70/30	48/52	12.5	258
P1-55	60/40	45/55	6.9	229
P1-67	50/50	33/67	8.4	138
P1-77	40/60	23/77	5.9	84
P1-78	30/70	22/78	3.2	79
P2-40	80/20	60/40	13.1	420
P2-51	70/30	49/51	12.8	269
P2-52	60/40	48/52	6.9	258
P2-76	50/50	24/76	15.2	88
P2-77	40/60	23/77	13.6	84
P2-88	30/70	12/88	11.2	38

This difference can be explained by the difference between the reactivity ratios of VIm and the methacrylate group. On the basis of reported data in the literature for the *N*-vinylimidazole/ethyl methacrylate (VIm/EMA) radical copolymerization system (r(VIm) = 0.35 and r(EMA) = 3.47),[25] apparently higher macromolecular PPGDMA cross-linker ratio can be expected in the conetworks than in the feed, on the one hand. On the other hand, considering that the product of the two reactivity ratios is close to one, random copolymerization can be expected.[13(b,c)] As the data in Figure 1 and Table 1 also reveal, there is a well-defined correlation between the VIm/PPGDMA feed ratio and the composition of the resulting PVIm-*l*-PPG conetworks. This affords designing and thus preparing of such conetworks with predetermined compositions.

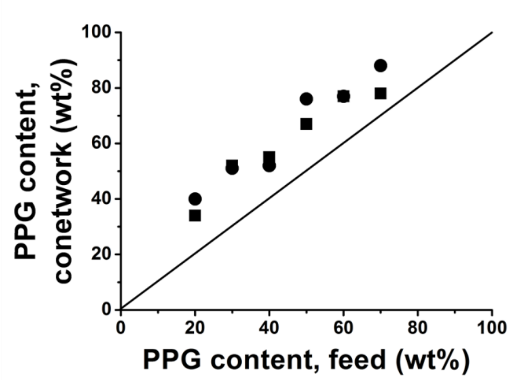


Figure 1. Poly(propylene glycol) (PPG) content of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-l-PPG) conetworks as a function of PPGDMA content in the feed (the solid line indicates 1/1 incorporation of PPG in the conetworks; (■) P1 series, (●) P2 series).

Thermal analysis and morphology. In order to get information on the fundamental phase behavior (phase separation or miscibility) of the components and the thermal stability of the PVIm-*l*-PPG conetworks, DSC and TGA measurements were carried out, respectively. Figure 2 shows the DSC thermograms of the PVIm-*l*-PPG conetworks, the PVIm homopolymer and the PPG macromolecular cross-linker. In these curves, the T_g values are denoted with small arrows. As shown in this Figure, the hydrophobic PPG homopolymer has a T_g at -76 °C and the hydrophilic PVIm glass transition can be found around 171 °C. Surprisingly, all the PVIm-*l*-PPG conetworks exhibit only one single T_g varying with the composition between that of the two homopolymers. This observation is in sharp contrast to the separate two glass transitions caused by nanophase separation of the components in amphiphilic conetworks reported so far. For APCNs, the existing results, in line with expectations, indicate phase separation between the immiscible hydrophilic and hydrophobic (or fluorophilic) chains.[2(a,d-f,h),3,6(a-d,f),8(b),10,11(a,c)12c,13c] Generally, if polymers with different philicities, such as hydrophilic and hydrophobic macromolecules, are combined in one cross-linked system, that is in a polymer conetwork, phase separation occurs at the nanoscale between the components due to the thermodynamically incompatible polymer chains, and two separate T_gs near to that of the homopolymers appear in the DSC curves. To test the miscibility of PVIm and PPG homopolymers, solvent casting was carried out with different PVIm/PPG compositions (20-80 wt% PPG; see Table S1) and DSC measurements were carried out with these blends. As shown in Figure S2 (in the Electronic Supplementary Information), hazy films were obtained in all the cases indicating phase separation of PVIm and PPG in these polymer mixtures. This was verified by DSC measurements as shown in Figure S3 and Table S2. Two separate glass transitions can be seen for each PVIm-*blend*-PPG mixtures with T_gs very close to that of the homopolymers. These findings definitely prove that the PVIm and PPG homopolymers are immiscible. However, as already mentioned on the basis of results displayed in Figure 2, these polymers become miscible in the PVIm-*l*-PPG conetworks, i. e. they have only one T_g, with a broader transition than that of the homopolymers, and there is no sign of glass transitions in the ranges of the homopolymers in the DSC curves even with relatively high PPG or VIm contents.

The T_g values of the PVIm-*l*-PPG conetworks are plotted as a function of the PPG content in Figure 3. As the data in this Figure show, the glass transition temperatures of the conetworks fall between the Tg of the pure homopolymers, closer to that of PVIm, and decrease with increasing hydrophobic PPG content. This Figure also shows that the two T_g values of the PVIm/PPG homopolymer blends correspond to the transitions of the neat homopolymers indicating that these two polymers are not compatible with each other (see also Figure S3 and Table S2 in the Electronic Supplementary Information).

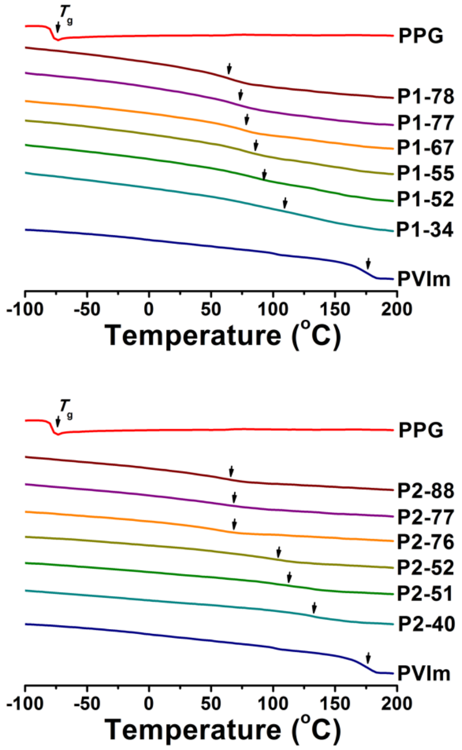


Figure 2. Differential scanning calorimetry (DSC) thermograms of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks, PVIm and PPGDMA macromolecular cross-linker. The glass transition temperature (T_g) values are indicated by small arrows.

Thus, it is obvious that the single T_g of the PVIm-*l*-PPG conetworks contradicts the expectations based on the immiscibility of the free-standing homopolymers in blends and on the results published on two T_gs for other amphiphilic conetworks so far.[2(a,d-f,h),3,6(a-d,f),8(b),10,11(a,c)12c,13c] For the sake of having some insight into the reasons of this striking observation in Figure 3, the measured Tgs are compared to the data expected on the basis of the Fox equation[26] derived for compatible blends ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$, where T_g, T_{g1}, T_{g2}, w_1 and w_2 stand for the glass transition temperatures of the blend, the first and second homopolymers and the corresponding weight fractions, respectively). The simple additive rule for the T_g of compatible blends is also depicted in this Figure. It is evident from the data in Figure 3 that neither the Fox equation nor the additive rule for the T_gs of the compatible blends fit with the measured glass transition temperatures of the PVIm-*l*-PPG conetworks. The evolved single T_gs are higher than the predicted values, which can be attributed to the molecular vicinity of the relatively short immiscible polymer chains with high and low T_gs resulting in the inhibition of the molecular motion of the polymer chain segments in the polymer with low T_g (PPG) and to the plasticizing effect of this polymer on the glassy PVIm component, due to the decreased free volume by reason of the dense conetworks.

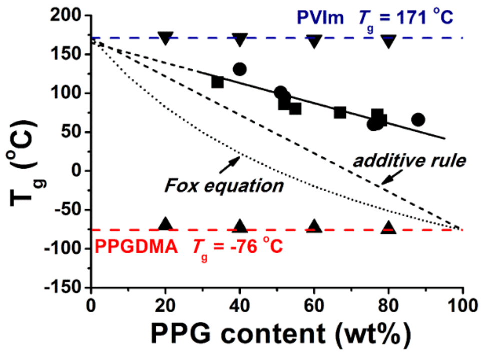
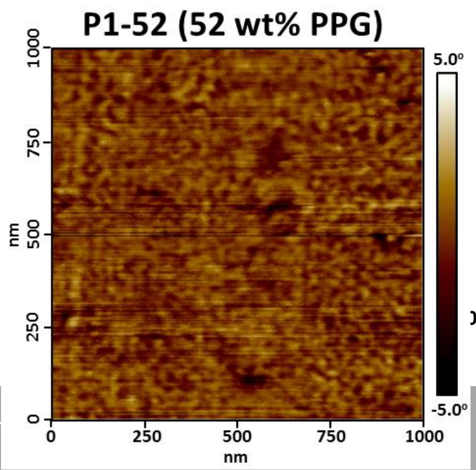


Figure 3. Glass transition temperatures (T_g) of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks and poly(*N*-vinylimidazole)-*blend*-poly(propylene glycol) (PVIm-*blend*-PPG) as a function of PPG content ((■) P1 and (●) P2 PVIm-*l*-PPG conetwork series, and (▲) PVIm and (▼) PPGDMA homopolymers in the PVIm-*blend*-PPG). The dotted black curve shows the calculated T_g by the Fox equation and the short dashed line indicates the T_gs according to the additive rule. The horizontal lines represent the T_g of the PVIm homopolymer (blue dashed line; 171 °C) and the PPGDMA macromolecular cross-linker (red dashed line; -76 °C).

The single T_g also indicates strong interpolymer interaction on molecular level between the PVIm and PPG chains in the random densely packed APCNs. It is noteworthy to mention that the intercept (165.2 °C) of the T_g versus composition plot results in an acceptable approximation of the measured T_g of the PVIm homopolymer (171 °C). It is also important to emphasize that even low amounts of VIm (12 wt%) is sufficient to obtain a conetwork with only a single glass transition and to have a material with a T_g (75 °C) high above the Tg of the elastic PPG (-76 °C). In connection to these findings, DSC experiments were carried out by us with mixtures with broad composition ranges of VIm monomer and PPGs having molecular weight in the range of 425-1000, to test whether the VIm monomer itself may lead to substantial T_g change of PPG. It was found that the presence of VIm has only negligible effect on the glass transition temperature of PPG. Evidently, these results also support that the single T_g observed in the PVIm-*l*-PPG conetworks high above that of the PPG component can be attributed to the chain-chain interaction in these new cross-linked bicomponent polymeric materials. These findings are substantial from application point of views and may open new routes for designing and preparing new bi- or multicomponent macromolecular materials with desired properties, such as novel single T_g macromolecular assemblies consisting of otherwise immiscible polymer chains.

The morphology investigation results obtained by phase mode AFM and TEM measurements of the PVIm-*l*-PPG conetworks corroborate the assumption that the two polymer chains are located in mixed phases forced by the covalent linkages between the relatively short chains of the components (Figures 4 and Figures S4 and S5 in the Electronic Supplementary Information). As it can be seen from the vertical range in the AFM phase images, only a minor diffuse tone difference can be observed, which is typically affected by sectioning of homogeneous polymers with T_g higher than room



temperature. Even a more diffuse picture without any sign of distinct phase separation is obtained by TEM (Figure S5). This small phase contrast indicates the existence of similar mixed phases with slightly different compositions, that is the lack of noticeable phase separation in all the PVIm-*l*-PPG conetworks. This is in accordance with the DSC results in Figures 2 and 3, i. e. with the relatively broad glass transitions and the single T_g which is due to the strong effect of the conetwork composing chains to each other's chain segment mobility in these densely packed conetworks with high cross-linking densities. It is noteworthy that only few cases are known when conetworks composed of oppositely polar components possess only one glass transition temperature.[3a,27]

Figure 4. Representative atomic force microscopy (AFM) phase mode image of the cross section (bulk morphology) of a poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetwork sample with 52 wt% PPG content (picture dimensions 1 µm x 1 µm). The vertical range is 10° for the phase image.

For instance, it was found by Bruns and Tiller that poly(1H,1H,2H,2Hheptadecylfluorodecyl acrylate)-*l*-poly(di-methylsiloxane) (PHDFDA-*l*-PDMS) (hydrophobic/ fluorophilic) conetworks with three glass transitions show only one T_g after heating above 100 °C and subsequent quick quenching in liquid nitrogen.[3a] In these conetworks, relatively short PDMS cross-linker with ~1000 g mol^{-1} average molecular weight was used. It is therefore plausible to conclude that due to the influence on each other segmential mobility of the components in conetworks with relatively high cross-linking densities (low M_c), i. e. due to the restriction of the freedom of movement on the segmential scale,[28] conetworks composed of otherwise immiscible polymers with relatively short chain length possess only a single glass transition.

The thermal stability is of great importance not only in the light of the observed single T_g, but from the point of view of potential applications of these materials as well. To compare the effects of temperature change on the homopolymers and APCN samples and their weight loss, TGA measurements were performed. Figure 5 shows the TGA and differential TGA (DTG) curves of the PVIm-*l*-PPG conetworks and both of the hydrophilic PVIm homopolymer and the hydrophobic PPG cross-linker under nitrogen atmosphere (see also Figure S6 in the Electronic Supplementary Information).

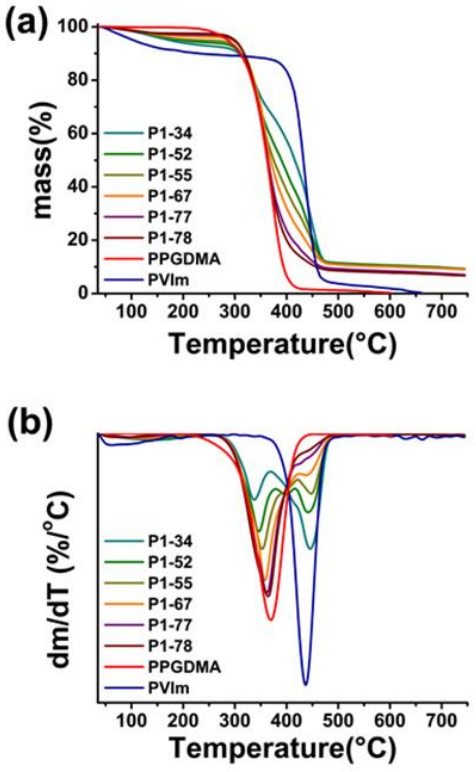


Figure 5. Thermogravimetric analysis (TGA) (a) and differential TGA (DTG) (b) curves of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks, PVIm homopolymer and PPGDMA macromonomer (under nitrogen with 10 °C·min^{-1} heating rate).

The temperature at the maximum rate of decomposition ($T_{d(max)}$) and char residue ($wt_{R(500)}$) at 500 °C (the solvent content of the conetworks were taken into account for a better comparability of the results) are listed in Table 2. On the one hand, the TGA and DTG curves show that the thermal degradation of the pure PPG homopolymer occurs in a one-step degradation process with a sharp weight loss between 275 and 425 °C with a maximum rate of weight loss at 362 °C, and this process leads to near complete decomposition with negligible char residue.[29] On the other hand, in the case of the PVIm homopolymer prior to the major one-step degradation process, the TGA curves also show a slight weight loss about 8-10% below 250 °C, which could be attributed to the evaporation of the absorbed water or solvents, such as acetone. The main thermal decomposition of PVIm takes place between 350 °C and 500 °C with a maximum decomposition rate at 437 °C and with a char residue of 4.1% at 500 °C.[13a] It can be seen in Figure 5 and Table 2 that the components of the PVIm-*l*-PPG conetworks compared to the neat polymers surprisingly keep their chemical integrity separately, at least to certain extent, in spite of their forced miscibility in the conetworks as the DSC and AFM results indicate. The thermal decomposition of the cross-linked PVIm-*l*-PPG conetworks undergoes in two major stages but without well-separable decomposition steps and with significant transition in between the decomposition temperatures of the two homopolymers ($T_{d(max)}$ = 362 °C for the PPGDMA macrocross-linker and $T_{d(max)}$ = 437 °C for the PVIm homopolymer), as shown in Figure 5. The temperatures ($T_{d(max)}$) of the two separate maximum rate of weight losses in the DTG curves of the conetworks are close to that of the corresponding PPG and PVIm homopolymers, but with considerable composition dependence as the data indicate in Table 2. The TGA curves in Figure 5 and the data in Table 2 also reveal that the VIm containing conetworks have considerable amounts of char residue in the range of 9-13% at 500 ^{o}C.

The thermograms of the conetworks show two decomposition stages, the $T_{\mathrm{d(max)}}$ for the first and second stages are between 334 and 366 and between 440 and 448 °C, respectively. The $T_{\mathrm{d(max)}}$ values belonging to the PPG increase with increasing PPG content, while the $T_{\mathrm{d(max)}}$ at higher temperatures is slightly higher than that of the PVIm homopolymer with $T_{\mathrm{d(max)}}$ of 437 °C. These results indicate that the presence of the polar VIm monomer units decreases the thermal stability of PPG, and in contrast, the PPG increases the PVIm's final decomposition temperatures to some minor extents. As a consequence, lower the PPG content, i. e. higher the PVIm ratio, lower the $T_{\mathrm{d(max)}}$ of the PPG as shown by the data in Table 2, on the one hand. On the other hand, the slight increase of the $T_{\mathrm{d(max)}}$ of PVIm in the conetworks is presumably due to termination of the radical decomposition of this polymer by the radicals formed during the PPG heterolytic scission. Based on our recent results with other VIm-containing conetworks,[13a] the ester linkage between the PPG cross-linker and the PVIm chains is considered as thermally labile point in the conetworks. The decomposition of the esters by *cis*-elimination accompanied by the heterolytic degradation of the PPG chains most likely plays an important role in the transitional temperature range. The transition period of thermal decomposition belongs to relatively large extent of mass loss as displayed in Figure 5. This indicates that the decomposing chains in these densely packed chemically forced conetworks significantly influence each other's decomposition, similar to that observed in poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) conetworks.[23a] This means that the radicals formed by the heterocyclic scission of the PPG chains may induce degradation of the PVIm segments as well. The data from the TGA analyses show that both the PPGDMA macromolecular cross-linker and the PVIm homopolymer possess low char yield (0.5% for PPGDMA and 4.1% in the case of PVIm), while PVIm-*l*-PPG conetworks (9.4-13.0%) have higher constant weight around 500 ^{o}C after complete thermal decomposition as shown in Table 2.

Table 2. The decomposition temperatures ($T_{\mathrm{d(max)}}$) and the weight percentage of char residues ($wt_{R(500)}$) of poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks and the neat polymers, PVIm homopolymer and PPGDMA macrocross-linker, respectively.

Sample ID	$T_{\mathrm{d(max)1}}$ (^{o}C)	$T_{\mathrm{d(max)2}}$ (^{o}C)	$wt_{R(500)}$ (%)	$wt_{R(500)}$(PVIm) (%)
P1-34	339	444	11.9	18.0
P1-52	348	444	11.9	24.8
P1-55	354	445	11.7	26.0
P1-67	357	446	11.2	34.1
P1-77	363	444	9.9	43.2
P1-78	366	-	9.4	42.6
P2-40	334	440	13.0	21.6
P2-51	335	440	12.4	25.4
P2-52	339	447	12.3	32.5
P2-76	356	444	10.5	43.8
P2-77	361	447	10.7	46.6
P2-88	360	448	10.5	87.2
PVIm	-	437	4.1	4.1
PPGDMA	362		0.5	-

$T_{\mathrm{d(max)}}$ (^{o}C): temperature of maximum rate of weight loss; $wt_{\mathrm{R(500)}}$ (%): weight percentage of residue at 500 °C; $wt_{\mathrm{R(500)}}$(PVIm) (%): weight percentage of residue related to PVIm content at 500 °C

For the comparison, the data for which the solvent contents were taken into account and were normalized to the PVIm content are also shown in this Table. It is evident from these data that the solid residue in the conetworks normalized to the VIm content monotonously increases with the decreasing amounts of the PPG cross-linker. This increased amount of the $wt_{\mathrm{R(500)}}$ in the case of the conetworks can be explained by the elimination of the hydrophilic compound's functional groups, acting as retardant on the scission of the conetwork.[29]

Hydrophilic and Hydrophobic Swelling. Swelling studies of the PVIm-*l*-PPG conetworks were carried out in both polar (water) and nonpolar (THF) solvents as well as the swelling behaviour was examined in ethanol, a common solvent for both components. The equilibrium swelling degrees (Q) are depicted in Figure 6 as a function of the hydrophobic PPG content in the conetworks.

The swelling behavior in nonpolar solvent for the samples with high PPG content (at 77 to 88 wt%) reaches around 209 and 216% swelling, while at low PPG content the Q values are 18 and 31%. The hydrophilic swelling shows the opposite trend, that is with decreasing PPG content the swelling degrees of the APCNs increase in water up to 160-180% with only 34-40 wt% PPG content. It should be noted, that the swelling in both solvents shows not usual behavior of APCNs reported so far. Relatively high swelling ratios are observed for a broader than usual conetwork composition in both water and THF. This is accordance with the homogeneous distribution of the composing polymer chains in these conetwork, that is with the ability of the solvent to reach most of the chains without phase barrier independent of composition. The not typical swelling behavior in water might be also due to the partial compatibility of the hydrophobic PPG with aqueous media[30] (see Figure S7 in the Electronic

Supplementary Information), which may facilitate the swelling in water, and thus it has an increasing effect on the swelling degree of the conetworks. The swelling in ethanol (Figure 6) reveals that this common solvent for both components used in the copolymerization is a suitable swelling media for the conetworks by interacting with both components. Thus, the swelling degree in ethanol is higher compared to the swelling in aqueous media. These swelling results show that the PVIm-*l*-PPG conetworks are able to swell in both polar and nonpolar solvents (Figure 6) even in spite of the densely mixed components. Consequently, the conetworks possess amphiphilic character, since the conetworks are able to act as hydrogels in water and as hydrophobic gels (organogels) in hydrophobic solvents. It is also shown that the swelling of the non phase-separated structure PVIm-*l*-PPG conetworks are composition dependent, meaning that higher the PPG content, higher the Q values in the nonpolar solvent and vica versa for the polar solvent. This dual, that is the amphiphilic character of these novel conetworks can be utilized in a various unique application possibilities, ranging from biomedicine to nanotechnologies.

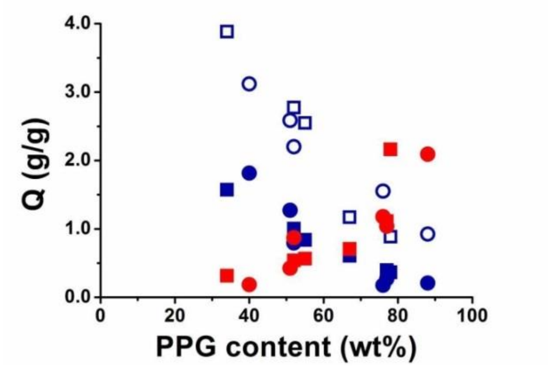


Figure 6. Equilibrium swelling ratios (Q) of the poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks ((■) P1 and (●) P2 PVIm-*l*-PPG conetwork series) as a function of the PPG content in nonpolar (THF, closed red color) and polar (water, closed blue color and ethanol, open blue color) solvents

Conclusions

The conclusions section should come in this section at the end of the article, before the acknowledgements. A series of novel poly(*N*-vinylimidazole)-*l*-poly(propylene glycol) (PVIm-*l*-PPG) conetworks were successfully synthesized by using the macromonomer method via free radical copolymerization of a low molecular mass monomer (VIm) with PPGDMA as macromolecular cross-linker with methacrylate functional end groups. The composition of the resulting APCN series varied between 34 and 88 wt% of PPG, by changing the ratio of the hydrophilic monomer and the hydrophobic macromolecular cross-linker in the feed. DSC analyses revealed that the PVIm-*l*-PPG conetworks exhibit only single glass transition between the T_gs of the corresponding homopolymers, indicating the formation of chemically forced miscibility of the short chain polymers in the densely packed PVIm-*l*-PPG conetworks composed of chains with close molecular vicinity. These findings corroborate the results of phase mode AFM and TEM measurements indicating the presence of mixed phases with slightly different compositions. TGA measurements revealed that the non phase-separated PVIm-*l*-PPG conetworks are stable up to high temperatures (around 350 °C), and the decomposition of the APCNs take place in two, but not well-separable stages, showing that the composing polymers keep their chemical integrity in the conetwork structure to certain extents, and simultaneously interact with each other's decomposition process. Although the immiscible components in the PVIm-*l*-PPG APCNs do not from disctinct separate phases, the results of swelling experiments conclusively indicate the amphiphilic nature of these new conetworks, i. e. these materials are able to swell in both hydrophilic (water and ethanol) and hydrophobic (THF) solvents, and the swelling degrees can be well controlled with composition.

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