Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

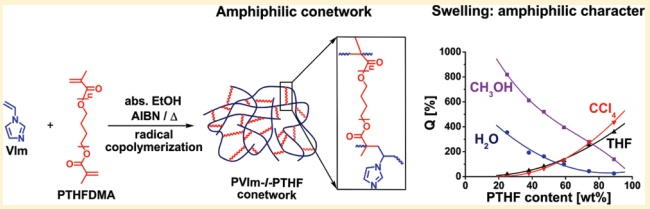
Poly(*N*-vinylimidazole)-*l*-Poly(tetrahydrofuran) Amphiphilic Conetworks and Gels: Synthesis, Characterization, Thermal and Swelling Behavior

Csaba Fodor, Gergely Kali, and Béla Iván*

Department of Polymer Chemistry and Material Science, Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri u. 59-67, P.O. Box 17, H-1525 Budapest, Hungary

Supporting Information

ABSTRACT: A novel class of amphiphilic conetworks (APCNs), poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) ("*l*" stands for "*linked by*"), was prepared by free radical copolymerization of telechelic PTHF dimethacrylate macromonomer and *N*-vinylimidazole in ethanol as a suitable cosolvent for all the components. Low amounts of extractables were obtained indicating successful conetwork formation. A series of transparent, macroscopically homogeneous PVIm-*l*-PTHF conetworks with a wide composition range of 25−89 wt % PTHF were prepared. Investigations by DSC revealed the existence of two distinct glass transition temperatures (T_g) in the vicinity of the T_g of homopolymers proving microphase separation of PVIm and PTHF in these conetworks. Surprisingly, the crystallization of PTHF is strongly suppressed and prevented at lower than 38 wt % PTHF in the presence of the glassy, amorphous PVIm in these APCNs. The amphiphilic nature of the PVIm-*l*-PTHF conetworks was proved by their uniform swelling in both nonpolar (tetrahydrofuran, carbon tetrachloride) and polar solvents (water, methanol) in a broad composition range, indicating bicontinuous (cocontinuous) phase separation in these novel, unique bicomponent polymeric materials.



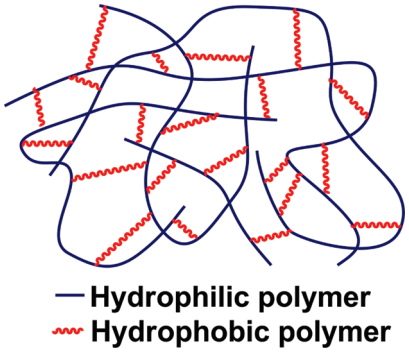
1. INTRODUCTION

Imidazole and its derivatives play a crucial role in biomacromolecules of living organisms (e.g., in proteins and nucleic acids) as well as in chemistry and in the chemical industry. For instance, its applications range from catalysts and ionic liquids to pharmaceutical compounds and a variety of specialty chemicals. Synthetic polymers with imidazole moieties, especially polymers containing vinylimidazole and benzimidazole, have recently received significant interest in order to utilize the unique chemical properties of the imidazole ring, e.g., as component in fuel cells[1] and metal ion complexing membranes,[2] gene delivery vectors,[3] electrophoresis medium,[4] ion imprinted matrices,[5] enzyme immobilization carrier,[6] corrosion protective coatings,[7] polyampholyte microgels,[8] catalysts,[9] and catalyst supports,[10] etc. These recent examples clearly indicate that poly(*N*-vinylimidazole) (PVIm) is a versatile polymer, and it possesses a variety of unique properties and provides several new application possibilities. Although conventionally cross-linked PVIm has been prepared and studied in recent years,[11−15] the structural and thus property variation and the mechanical stability of such hydrogels are rather limited. Considering the recent rapid developments in the field of amphiphilic conetworks,[16−46] PVIm-based conetworks are expected to lead to a number of novel materials with interesting structures and properties. However, according to the best of our knowledge, amphiphilic conetworks and gels with PVIm as the hydrophilic component have not been reported yet.

Amphiphilic conetworks (APCN)[16−46] belong to a rapidly emerging class of novel nanophasic macromolecular systems. A polymer conetwork in general consists of at least two different polymer chains connected with chemical bonds to each other. APCNs are specifically composed of chemically bonded, otherwise immiscible hydrophilic and hydrophobic macromolecules. Such a cross-linked macromolecular assembly, in which one of the polymer chains serves as the cross-linker for the other polymer, is depicted in Scheme 1. These materials are able to swell in and interact with both hydrophilic and hydrophobic solvents and materials, respectively. As a consequence, APCNs behave as either specialty hydrogels or hydrophobic gels depending on the nature of the swelling medium.[34] It has also been found by a variety of techniques, such as DSC, TEM, AFM, SAXS, SANS, and solid-state NMR, that the polymeric components form separated nanodomains in APCNs.[21−23,25,28,46c,46d] Over the past few years, special attention has been paid to these novel unique materials due to their special nanostructures and properties. As a consequence, wide ranges of potential applications of APCNs, such as controlled drug release matrices,[27,31−34] biomaterials,[19e,35,36] tissue engineering scaffolds,[37,38] immunoisolation membranes,[39] contact lenses,[40,41] pervaporation

Received: March 26, 2011
Revised: April 28, 2011
Published: May 06, 2011

Scheme 1. Amphiphilic Conetwork (APCN) Structure Consisting of Chemically Bonded Hydrophilic and Hydrophobic Polymer Chains (Hydrophobic Polymer Is Depicted as Cross-Linker)



membranes,[42] antifouling surfaces,[29c,43] enzymatic catalysis supports,[30] sensors,[44] and nanoreactors or nanotemplates of nanohybrids,[21,30] have already been investigated. Utilizing one of the nanophases as nanoreactor has yielded novel nanohybrid materials with nanocrystalline inorganic particles.[21] These examples indicate that the unique properties of APCNs make them useful in many different fields, such as medicine, optics, catalysis, electronics, sensors, actuators, mechanics, etc.[16a,19a]

We have aimed at the synthesis of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) ("*l*" stands for "*linked by*") APCNs, that is, combining the hydrophilic PVIm with the hydrophobic PTHF in one single network structure, followed by investigating the properties of the resulting new materials. Methacrylate−telechelic poly(tetrahydrofuran) (PTHFDMA) was selected as the hydrophobic macromolecular cross-linker. Attempts for APCN synthesis by PTHFDMA in conjunction with acrylic acid/amide,[45a−c] methacrylic acid,[45e] and isopropylacrylamide[45e] have recently been reported. The resulting conetworks were characterized in terms of their swelling behavior and thermal properties.[45] On the other hand, PTHF is one of the best biocompatible polymers[47] with low immunogenicity among the polymeric materials used in medical applications nowadays. Thus, considering the advantageous and unique properties of PVIm and PTHF, we have attempted to connect these two macromolecules into amphiphilic conetwork structures. Herein, we report on the synthesis and characterization of a series of new cross-linked macromolecular architectures, PVIm-*l*-PTHF amphiphilic polymer conetworks.

2. EXPERIMENTAL SECTION

2.1. Materials. *N*-Vinylimidazole (VIm, Aldrich) was vacuum-distilled from CaH_2 (95%, Aldrich) at 72 °C and kept under nitrogen until used. Hydroxyl-ended poly(tetrahydrofuran) (Terathane 2000 polyether glycol, PTHF, average $M_n \sim 2000$) was purchased from Fluka. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Aldrich) was recrystallized from methanol before use. Triethylamine (Et_3N, ≥99.5%) and methacryloyl chloride (MACl, ≥97%) were purchased from Fluka and were distilled under vacuum (Et_3N room temperature, MACl 30−32 °C). Dichloromethane (DCM, 98%, Scharlau) was refluxed over CaH_2 (95%, Aldrich) and freshly distilled before use. *n*-Hexane (96%, Scharlau) was stored over concentrated H_2SO_4 (Freak, Ltd.) and then was passed through a basic aluminum oxide (99%, Aldrich) column to remove the acidic impurities. Finally, it was refluxed over CaH_2 and freshly distilled before use. Freshly distilled absolute ethanol and benzene (Spektrum 3D) were used as solvents for the copolymerization and homopolymerization, respectively. Methanol (99.97%, Spectrum 3D), acetone (Molar Chemicals Ltd.), tetrahydrofuran (min. 99%, Spectrum 3D), and carbon tetrachloride (Chemolab Ltd.) were used as received. Distilled and deionized water was used in experiments with water.

2.2. Preparation of PVIm Homopolymer. The PVIm homopolymer was synthesized by radical polymerization 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 ^{1}H NMR spectroscopy.

2.3. Preparation of PVIm-*l*-PTHF Conetworks. First, the macromolecular PTHFDMA cross-linker was prepared by reacting α,ω-dihydroxy poly(tetrahydrofuran) (PTHFDOH) with methacryloyl chloride (synthesis details and analysis data of PTHFDMA are given in the Supporting Information). The resulting methacrylate−telechelic PTHF (PTHFDMA) was characterized by GPC ($M_n = 2170$, $M_w/M_n = 1.65$) and by ^{1}H NMR for end-group functionality ($F_n = 2.0$). The APCN samples were prepared by carrying out free radical copolymerization of VIm using PTHFDMA as cross-linker and AIBN as initiator as it is shown in Scheme 2. For the synthesis of APCNs, the desired amounts of the cross-linking agent and comonomer of 1 g of total mass, initiator stock solution, and common solvent, EtOH, were measured into glass vials. The total volume of the solutions was 6 mL. Table 1 shows the applied ratios of the components. The AIBN concentration was adjusted to the total concentration of the comonomers in order to keep the $[\text{comonomer}]/[\text{AIBN}]^{0.5}$ ratio constant at 0.988 value. The reaction mixtures were homogenized, and the oxygen was removed by nitrogen purging. The solutions were poured into Teflon molds in an AtmosBag (Sigma-Aldrich) under a nitrogen atmosphere. Then the molds were closed under nitrogen and kept in an oven at 65 °C for a period of 3 days. Subsequently, the molds were cooled to room temperature, and the solvent was evaporated, followed by drying the conetworks under vacuum overnight. The resulting cross-linked polymers were extracted with tetrahydrofuran (THF) and methanol (MeOH) for 1 week with both solvents. The amounts of extractables were determined gravimetrically by evaporating the solvents followed by drying the residues to constant weight in vacuo. Finally, the extracted conetworks were dried to constant weight under vacuum at 50 °C.

2.4. Methods. ^{1}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 research. ^{1}H NMR spectra were obtained on a Varian Unity INOVA spectrometer operating at ^{1}H frequency of 400 MHz. Samples were dissolved in appropriate deuterated solvents ($CDCl_3$, DHO). TMS at 0 ppm and $CDCl_3$ at 7.28 ppm were used as internal reference for ^{1}H NMR.

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.

Mettler TG50 instrument was used for differential scanning calorimetry (DSC) analysis to determine the glass transition temperatures of the synthesized polymers. The midpoint of the specific heat increase in the transition region during the second heating is reported as the glass transition temperature (T_g). Programmed heating cycles from −120 to 200 °C were used at a heating rate of 10 °C/min under a nitrogen atmosphere.

Scheme 2. Formation of Poly(*N*-vinylimidazole)-*l*-Poly(tetrahydrofuran) (PVIm-*l*-PTHF) Conetwork by Radical Copolymerization of *N*-Vinylimidazole (VIm) with Telechelic Poly(tetrahydrofuran) Dimethacrylate (PTHFDMA) Macromonomer

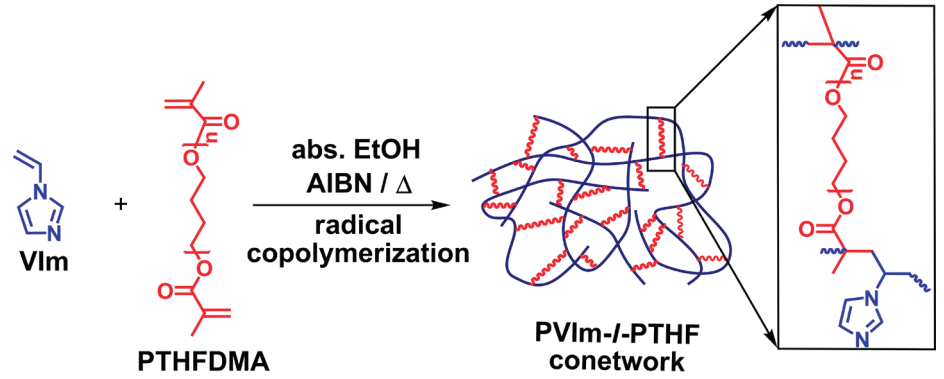


Table 1. Feed Ratios, Amounts of Extractables, Composition of the Conetworks and Average Molecular Weights (M_c) of PVIm in the Conetworks

		extractables (%)			
sample code	VIm/PTHF feed ratio (wt %)	THF	methanol	PVIm/PTHF in conetwork (wt %)	M_c of PVIm
V-25	80/20	1.3	9.2	75/25	3260
V-38	70/30	1.4	5.7	62/38	1770
V-47	60/40	1.1	4.5	53/47	1220
V-59	50/50	1.2	2.8	41/59	750
V-74	40/60	1.4	2.9	26/74	380
V-89	30/70	2.8	3.6	11/89	130

Swelling, that is solvent uptake ratios of the conetworks, was determined gravimetrically in nonpolar (THF, CCl_4) and polar (MeOH, H_2O) solvents. The experiments were carried out as follows: the dried polymer samples were placed in the selected solvent at room temperature and were left to swell until constant weight. The samples were removed from the solvent at certain time intervals, wiped with a filter paper and weighed, and then placed again in the solvent bath. The equilibrium swelling ratios (Q) were obtained at constant weight and 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.

3. RESULTS AND DISCUSSION

Synthesis of PVIm-*l*-PTHF Conetworks. In order to obtain conetworks between immiscible polymer chains by copolymerization of a telechelic macromonomer and a low molecular weight monomer, few basic requirements should be met in the course of the synthetic process.[34] First, the macromonomer should copolymerize with the monomer; that is, the copolymerization reactivity ratios should allow efficient copolymerization. Second, the kinetic chain length of the polymer formed from the low molecular weight monomer should be long enough for the incorporation of at least two cross-linking macromonomers. Third, and most importantly, phase separation between the components of such polymerization systems should be avoided during the conetwork preparation. Taking into account these requirements, the radical copolymerization of *N*-vinylimidazole (VIm) with PTHFDMA was carried out as shown in Scheme 2 by using various feed ratios in ethanol, a cosolvent for VIm, PVIm, and PTHF, at 65 °C with AIBN as initiator under a nitrogen atmosphere (see Table 1 for feed amounts). The control of the composition of the conetworks was attempted by varying the feed ratios of the VIm monomer and the macromolecular PTHFDMA cross-linker. Feed compositions with 30 to 80 wt % of cross-linker were copolymerized. After terminating the copolymerization by cooling to room temperature and opening the molds, gelation was observed in every case, indicating network formation. In order to determine the efficiency of the curing reaction, all the resulting materials were extracted with THF and subsequently with methanol for removing the unreacted hydrophobic PTHF and the hydrophilic VIm and PVIm, respectively, which did not incorporate into the conetworks. As shown in Table 1, the amounts of extractables are in the range of 4−10.5%. These low extractable values convincingly indicate successful conetwork formation by the applied process. As exhibited in Figure 1, transparent, macroscopically homogeneous samples were obtained in all cases. This means that macroscopic phase separation of the immiscible components, leading to opaque materials, is prevented by the covalent bonds between the hydrophilic and hydrophobic polymer chains in the conetworks.

As shown in Table 1, considerable deviations exist between the feed ratios and the composition of the resulting PVIm-*l*-PTHF conetworks, especially at lower VIm contents in the feed (for the

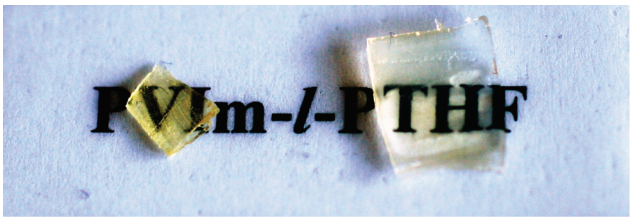


Figure 1. Transparent dry (left) and water swollen (right) poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) conetworks (sample V-47 in Table 1).

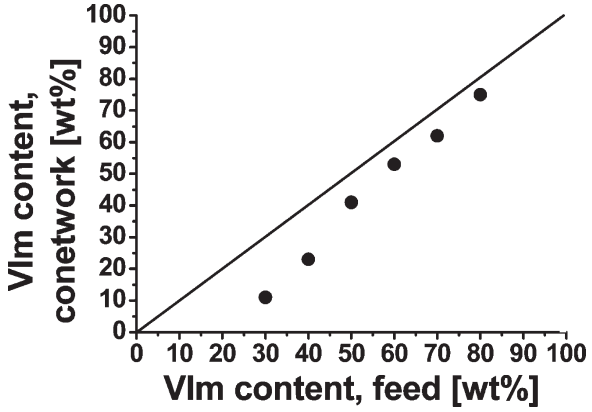


Figure 2. Composition of the PVIm-*l*-PTHF conetwork series: *N*-vinylimidazole (VIm) content in the conetworks as a function of the relative amount of VIm in the feed. The solid line represents 1:1 feed/conetwork composition.

sample codes in this table, V stands for the VIm component, while the numbers indicate the wt % PTHF content in the conetworks after extraction). The differences between feed ratios and conetwork compositions are better illustrated in Figure 2 displaying the relative amounts of PVIm in the conetworks as a function of the VIm content in the feed. The higher the amount of VIm in the feed, the closer the VIm content in the conetworks to the feed ratios. Taking into account that the reactivity ratios in the VIm/ethyl methacrylate (EMA) radical copolymerization[48] were found to be r_1 = 0.35 and r_2 = 3.47, nearly random copolymerization can be expected in the VIm/PTHFDMA system, on the one hand. However, due to the lower reactivity of VIm in this copolymerization, the resulting copolymers, the conetworks in our case, should contain less VIm than that in the feed. At higher VIm contents in the feed, the difference between the feed and conetwork compositions becomes smaller. This can be explained by the effect of the molecular weight, concentration, and viscosity of the macromonomer on the reactivity ratios. According to the findings by Müller et al.,[49,50] the apparent reactivity of the macromonomers decreases with the increasing molecular weight, concentration, and viscosity. Thus, the decreased reactivity of the PTHFDMA macromonomer compared to its low molecular weight counterparts, such as EMA, leads to higher VIm content in the conetworks than that expected on the basis of the reactivity ratios of the VIm/EMA copolymerization. This means that the physical effects on the apparent reactivity of the macromonomer in cases when the reactivity of its polymerizing group is higher than that of the comonomer are advantageous to obtain conetwork compositions closer to feed ratios. The higher deviations at high macromonomer concentrations,

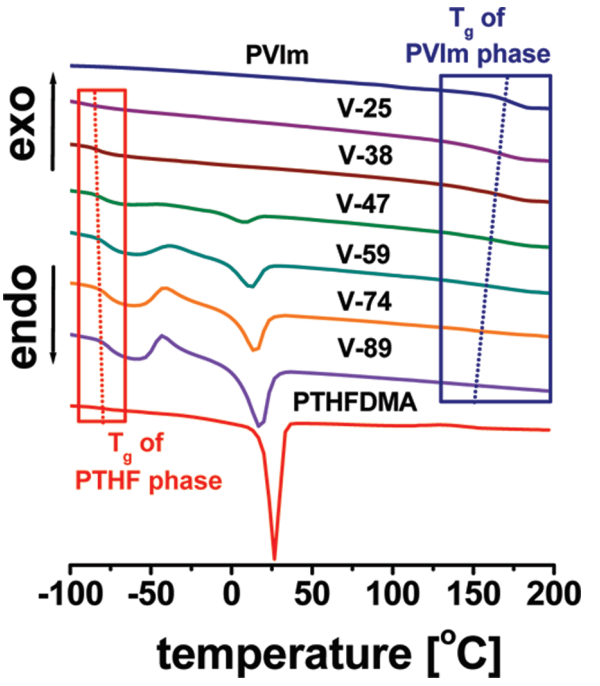


Figure 3. Differential scanning calorimetry thermograms (second scan) of PVIm-*l*-PTHF conetworks, poly(*N*-vinylimidazole) (PVIm), and poly(tetrahydrofuran) dimethacrylate (PTHFDMA).

like for samples with 74 and 89 wt % of macromonomer, can be due to imperfect copolymerization caused by the high viscosity of the feed.

The average molecular weights of the hydrophilic PVIm segments between two cross-linking points (M_c) in the conetworks were calculated by the following formula[34]

$$M_c = 0.5\frac{w_{PVim}}{w_{PTHF}}M_{PTHF}$$

where w_{PVIm}, w_{PTHF}, and M_{PTHF} stand for weight fraction of PVIm, the weight fraction of PTHF, and the number-average molecular weight of PTHFDMA, respectively. This estimation of M_c of PVIm in the conetworks does not consider loops or loose ends. As to lose ends, previous studies[34c] indicate negligible unreacted bismacromonomer cross-linker in the conetworks at high conversions; thus, complete incorporation of the bismacromonomer cross-linker in the extracted conetworks was taken into account for M_c calculation. On the other hand, it is an interesting structural aspect of these and similar conetworks that the M_c for the macromolecular cross-linker, that is, for PTHF in this case, is constant (2170 g/mol) in all the PVIm-*l*-PTHF conetworks. As given in Table 1, the M_c of PVIm changes from 130 to 3250 in the PVIm-*l*-PTHF conetworks. Obviously, the low M_c values for samples with 74 and 89 wt % PTHF reflect the high PTHF content and indicate that macromonomer coupling also occurs in these conetworks connected to relatively short PVIm segments.

DSC Analysis. In order to obtain information on the miscibility of components in the transparent PVIm-*l*-PTHF conetworks, DSC measurements were carried out. Figure 3 shows the DSC thermograms of the PVIm-*l*-PTHF series with varying compositions and of the homopolymers of PVIm and PTHF as well. The PTHF homopolymer has a glass transition temperature (T_g) at −87 °C and a melting peak at 25 °C due to the semicrystallinity of this homopolymer. The T_g of PVIm can be found at 171 °C. The DSC curves of all the PVIm-*l*-PTHF

dx.doi.org/10.1021/ma200700m |*Macromolecules* 2011, 44, 4496–4502

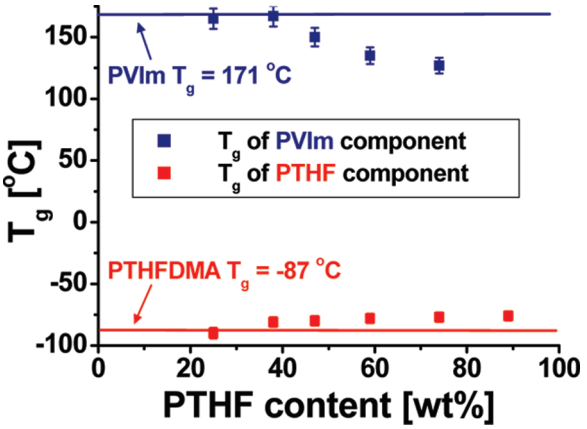


Figure 4. Glass transition temperature (T_g) values of PVIm-*l*-PTHF conetworks as a function of composition. The red line represents the T_g of the PTHFDMA macromonomer, and the blue line displays the T_g of the PVIm homopolymer.

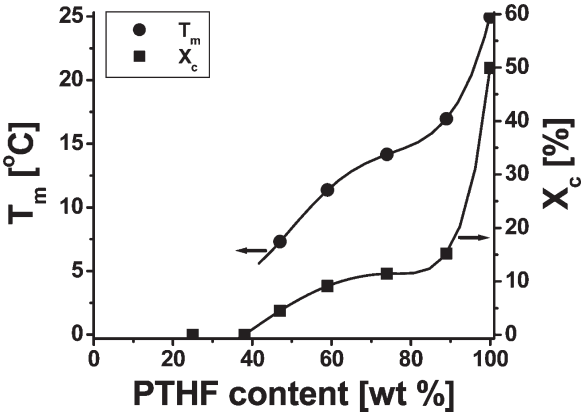


Figure 5. Melting point (T_m) and the extent of crystalline content (X_c) of poly(tetrahydrofuran) as a function of the relative amount of PTHF in the PVIm-*l*-PTHF conetworks.

conetwork samples exhibit two distinct glass transitions: one in the region of the T_g of PTHF and another one at around the T_g of PVIm. These findings clearly indicate that the two components, PVIm and PTHF, form separate domains in the PVIm-*l*-PTHF conetworks. This means that these conetworks can be considered as chemically forced blends between the immiscible PVIm and PTHF polymer chains, on the one hand. However, macroscopic phase separation is prevented due to the strong covalent bonds between these chains, on the other hand. The T_g values as a function of PTHF content are depicted in Figure 4. In this figure, an interesting tendency can be observed for the variation of T_gs with composition. The T_g of PVIm decreases, whereas the T_g of PTHF increases with increasing PTHF content in the conetworks. For PVIm, the T_g change is quite significant. It is 127 °C at 74 wt % PTHF, instead of 171 °C found for the PVIm homopolymer and conetworks with 25 and 38 wt % PTHF content. This indicates that PTHF has some plasticizing effect on PVIm at higher PTHF/PVIm ratios in these conetworks. Although the T_g increase of ~11 °C for PTHF at higher PTHF contents is not as high as the T_g change for PVIm, it is rather unexpected. The opposite tendency would be expected in case of

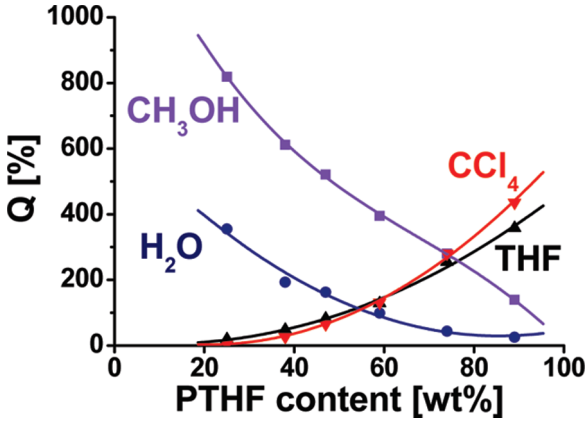


Figure 6. Equilibrium swelling ratios (Q) of the PVIm-*l*-PTHF conetworks as a function of the PTHF content in different nonpolar and polar solvents.

some extent of miscibility; i.e., higher T_g of PTHF in the conetworks should be observed at lower PTHF contents than that of the homopolymer.

The DSC curves in Figure 3 reveal another interesting phenomenon as well. Since PTHF is a semicrystalline polymer,[51] a melting peak at 26.6 °C is observed in the DSC scan of PTHFDMA. The formation of PTHF microcrystals was also expected to occur in the PVIm-*l*-PTHF conetworks. Indeed, the DSC thermograms (Figure 3) show exothermic peaks in the range of ~−40 °C, indicating crystallization and endotherms of melting for conetworks with relatively high PTHF contents. However, as shown in Figures 3 and 5, the melting temperatures (T_m) of PTHF are lower in the PVIm-*l*-PTHF conetworks than that of the homopolymer PTHF. The presence of just 11 wt % of PVIm decreases T_m of PTHF from 26.6 to 17 °C, and further T_m decrease takes place with increasing PVIm content, on the one hand. It can also be seen in Figure 3 that the height of melting peaks also decreases with the decreasing relative amounts of PTHF in the conetworks, and crystallinity cannot be observed in PVIm-*l*-PTHF samples with 25 and 38 wt % PTHF, on the other hand. Evaluation of the melting data shows that the crystalline ratio of PTHF (with 167 J/g enthalpy of melting[51] and normalized to the relative PTHF content) is also decreasing with decreasing PTHF content in the conetworks (Figure 5). A significant decrease of the crystalline phase, i.e., from 50% for PTHFDMA homopolymer to 15% for the conetwork sample with 89 wt % PTHF, was found followed by decreasing crystallinity with increasing PVIm content in the conetworks. These findings allow concluding that the crystallinity of PTHF is significantly suppressed in the PVIm-*l*-PTHF conetworks, and both the melting temperatures and the extent of crystallinity are composition dependent. The crystallization of PTHF is even completely prevented at lower than 38% PTHF content. Similar diminishing of the PTHF's melting peak was observed by Du Prez et al.[46b] for poly(*N*-isopropylacrylamide)-*l*-poly(tetrahydrofuran) conetworks. Suppression of crystallization of poly(ethylene glycol) (PEG) was also reported for PEG−polyisobutylene conetworks.[17] These results, that is, the significant decrease or lack of crystalline phases and the melting point suppression of PTHF in the PVIm-*l*-PTHF conetworks, might be important for applications in which crystalline phases are undesired in PTHF containing polymer products.

Hydrophilic and Hydrophobic Swelling: Hydrogel or Hydrophobic Gel as One Material. Swelling studies of the PVIm-*l*-PTHF conetworks were performed in nonpolar and polar solvents. It was found that transparent gels were formed by swelling in all cases (Figure 1); that is, the swelling process does not lead to large, scattering domains to make the materials opaque. In particular, the equilibrium swelling ratios (Q) were determined in carbon tetrachloride, tetrahydrofuran, methanol, and water. Figure 6 displays the swelling ratios in these solvents as a function of the hydrophobic PTHF content of the conetworks. The results of the swelling experiments in Figure 6 unequivocally show that the PVIm-*l*-PTHF conetworks are able to swell in both hydrophilic and hydrophobic solvents. This means that these materials behave as hydrogels in water and in other polar solvents and as hydrophobic gels in nonpolar solvents. In other words, the PVIm-*l*-PTHF conetworks indeed possess amphiphilic character. In water, only the hydrophilic PVIm phases are able to swell, while the hydrophobic PTHF phases of the conetworks interact with nonpolar solvents, such as carbon tetrachloride and tetrahydrofuran. In common solvents for both components, such as in methanol, both phases are able to swell. As a consequence, higher Q values are obtained in methanol than that in the other solvents as shown in Figure 6. It is also exhibited in this figure that the equilibrium swelling ratios strongly depend on composition. Higher the hydrophobic PTHF content, higher the Q values in hydrophobic carbon tetrachloride and tetrahydrofuran. This observation is the consequence of the increase of the PTHF content in the conetworks, and this cannot be related to the changes in the M_c of PTHF because it is a constant value of 2170 g/mol for all the investigated conetworks as presented in Scheme 2. An opposite tendency is observed for polar solvents, i.e., water and methanol. The higher the hydrophobic content, the lower the swelling ratios in polar solvents. It is also noteworthy that relatively high equilibrium swelling ratios are observed, that is, up to ~800% in methanol, ~370% in water, and ~500% in carbon tetrachloride and tetrahydrofuran. It has to be noted that further evaluation of the results of these swelling experiments is rather limited due to the fact that according to our knowledge realistic theoretical approaches for such three-component swollen polymer conetwork gel systems with liquid, swollen, and nonmiscible (nonswollen) polymeric phases do not exist at the present time.

The uniform swelling of both components, especially in the range of ~40−70 wt % PTHF content, in both polar and nonpolar solvents indicates that cocontinuous (bicontinuous) phase morphology exists in the PVIm-*l*-PTHF amphiphilic conetworks. Such broad composition window for uniform swelling in both kinds of solvents can be utilized for a variety of applications, for instance, by loading either the hydrophilic or the hydrophobic phases with desired compounds.

4. CONCLUSION

A series of novel poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) amphiphilic conetworks were successfully synthesized by free radical copolymerization of methacrylate−telechelic PTHF macromonomer with VIm comonomer in ethanol, a common solvent for all the components. The composition of the APCNs was varied between 25 and 89 wt % of PTHF by changing the ratio of the hydrophobic macromonomer and the hydrophilic comonomer in these copolymerizations. Low amounts of extractables were obtained indicating high extent of PVIm-*l*-PTHF conetwork formation. DSC analysis revealed that these new, transparent materials exhibit two distinct glass transitions in the range of the corresponding homopolymers. This allows to conclude the existence of phase separation in these conetworks. Thus, these new macromolecular conetwork assemblies can be viewed as molecularly forced blends between otherwise immiscible polymers. It was also found that the crystallization ability of the PTHF phase is strongly suppressed, and it is composition dependent. It is even completely diminished below 40 wt % PTHF content.

The hydrophilic and hydrophobic swelling behavior of the PVIm-*l*-PTHF conetworks, i.e., the amphiphilic nature of these new materials, was demonstrated by swelling in tetrahydrofuran and carbon tetrachloride as nonpolar solvents and in water and methanol as polar solvents. It was found that the equilibrium swelling ratios depend on the nature of the solvent and conetwork composition. The higher the hydrophobic content, the higher the swelling ratio in nonpolar solvents. In contrast, higher PTHF content results in lower hydrophilic swelling. It has to be emphasized that uniform swelling of high extent was observed in both kinds of solvents in a broad composition range, indicating bicontinuous (cocontinuous) microphase-separated structure in these bicomponent novel amphiphilic macromolecular architectures. In fact, one single material, i.e., the PVIm-*l*-PTHF conetwork, behaves as either a hydrogel or a hydrophobic gel depending on the nature of the philicity of the medium. This opens up a plethora of application opportunities ranging from medical fields to novel nanomaterials.

■ ASSOCIATED CONTENT

Supporting Information. Detailed synthetic procedure for the preparation of poly(tetrahydrofuran) dimethacrylate and analysis by ^{1}H NMR and GPC. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: bi@chemres.hu.

■ ACKNOWLEDGMENT

The authors are grateful for the elemental, thermal, and GPC analyses to Dr. H. Medzihradszky-Schweiger, Ms. J. Szauer, and Dr. M. Szesztay, respectively. Partial support of this research by the Hungarian Scientific Research Fund (OTKA K81592) and by the Nanomedicine Thematic Program of the Chemical Research Center of the Hungarian Academy of Sciences is also acknowledged.

■ REFERENCES

(1) (a) Guan, Y. S.; Pu, H. T.; Jin, M.; Chang, Z. H.; Wan, D. C. *Fuel Cells* **2010**, *10*, 973–982. (b) Guan, Y. S.; Pu, H. T.; Pan, H. Y.; Chang, Z. H.; Jin, M. *Polymer* **2010**, *51*, 5473–5481. (c) Tian, A. H.; Kim, J.-Y.; Shi, J. Y.; Kim, K. *J. Power Sources* **2008**, *183*, 1–7.

(2) (a) Bessbousse, H.; Rhlalou, T.; Verchere, J. F.; Lebrun, L. *J. Chem. Eng.* **2010**, *164*, 37–48. (b) Ajji, Z.; Ali, A. M. *J. Hazard. Mater.* **2010**, *173*, 71–74. (c) Özmen, F.; Kavlaki, P. A.; Güven, O. *J. Appl. Polym. Sci.* **2011**, *119*, 613–619.

(3) (a) Asayama, S.; Hakamatani, T.; Kawakami, H. *Bioconjugate Chem.* **2010**, *21*, 646–652. (b) Ihm, J. E.; Han, K. O.; Hwang, C. S.; Kang,

J. H.; Ahn, K. D.; Han, I. K.; Han, D. K.; Hubbell, J. A.; Cho, C. S. *Acta Biomater.* **2005**, *1*, 165–172.
(4) Li, J.; Han, H. F.; Wang, Q.; Liu, X.; Jiang, S. X. *J. Sep. Sci.* **2010**, *33*, 2804–2810.
(5) Tu, J.; Zhou, J.; Wang, C. F.; Zhang, Q. A.; Chen, S. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 4005–4012.
(6) Isikli, S.; Tuncagil, S.; Bozkurt, A.; Toppare, L. *J. Macromol. Sci., Pure Appl. Chem.* **2010**, *47*, 639–646.
(7) Yuan, S. J.; Pehkonen, S. O.; Liang, B.; Ting, Y. P.; Neoh, K. G.; Kang, E. T. *Corros. Sci.* **2010**, *52*, 1958–1968.
(8) Schachschal, S.; Balaceanu, A.; Melian, C.; Demco, D. E.; Eckert, T.; Richtering, W.; Pich, A. *Macromolecules* **2010**, *43*, 4331–4339.
(9) Beletskaya, I. P.; Tarasenko, E. A.; Khokhlov, A. R.; Tyurin, V. S. *Russ. J. Org. Chem.* **2010**, *46*, 461–467.
(10) Beletskaya, I. P.; Selivanova, A. V.; Tyurin, V. S.; Matveev, V. V.; Khokhlov, A. R. *Russ. J. Org. Chem.* **2010**, *46*, 157–161.
(11) Molina, M.; Gomez-Anton, M. R.; Pierola, I. F. *Macromol. Chem. Phys.* **2002**, *203*, 2075–2082.
(12) Pacios, I. E.; Pierola, I. F. *Macromolecules* **2006**, *39*, 4120–4127.
(13) Valencia, J.; Pierola, I. F. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1683–1693.
(14) Calvino-Casilda, V.; López-Peinado, A. J.; Vaganova, E.; Yitzchaik, S.; Pacios, I. E.; Pierola, I. F. *J. Phys. Chem. B* **2008**, *112*, 2809–2817.
(15) Pacios, I. E.; Pierola, I. F. *J. Appl. Polym. Sci.* **2009**, *112*, 1579–1586.
(16) (a) Patrickios, C. S.; Georgiou, T. K. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 76–85. (b) Pafiti, K. S.; Loizou, E.; Patrickios, C. S.; Porcar, L. *Macromolecules* **2010**, *43*, 5195–5204. (c) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4289–4301. (d) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. *Langmuir* **2007**, *23*, 10746–10755. (e) Georgiou, T. K.; Patrickios, C. S.; Groh, P. W.; Iván, B. *Macromolecules* **2007**, *40*, 2335–2343. (f) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. *Macromolecules* **2007**, *40*, 2192–2200.
(17) Erdödi, G.; Iván, B. *Chem. Mater.* **2004**, *16*, 959–962.
(18) (a) Mespouille, L.; Hedrick, J. L.; Dubois, P. *Soft Matter* **2009**, *5*, 4878–4892. (b) Mespouille, L.; Coulembier, O.; Paneva, D.; Degee, P.; Rashkov, I.; Dubois, P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 4997–5013. (c) Mespouille, L.; Coulembier, O.; Paneva, D.; Degee, P.; Rashkov, I.; Dubois, P. *Chem.—Eur. J.* **2008**, *14*, 6369–6378.
(19) (a) Erdödi, G.; Kennedy, J. P. *Prog. Polym. Sci.* **2006**, *31*, 1–18. (b) He, C.; Erdődi, G.; Kennedy, J. P. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 1474–1481. (c) Daum, J.; Erdődi, G.; Kennedy, J. P. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 4039–4052. (d) Daum, J.; Erdődi, G.; Kennedy, J. P. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 4053–4062. (e) Jewrajka, S. K.; Erdődi, G.; Kennedy, J. P.; Ely, D.; Dunphy, G.; Boehme, S.; Popescu, F. *J. Biomed. Mater. Res., Part A* **2008**, *87A*, 69–77.
(20) Haraszti, M.; Tóth, E.; Iván, B. *Chem. Mater.* **2006**, *18*, 4952–4958.
(21) Scherble, J.; Thomann, R.; Iván, B.; Mülhaupt, R. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1429–1436.
(22) Iván, B.; Almdal, K.; Mortensen, K.; Johannsen, I.; Kops, J. *Macromolecules* **2001**, *34*, 1579–1585.
(23) Domján, A.; Erdödi, G.; Wilhelm, M.; Neidhöfer, M.; Landfester, K.; Iván, B.; Speiss, H. W. *Macromolecules* **2003**, *36*, 9107–9114.
(24) (a) Zhu, C.; Hard, C.; Lin, C. P.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4017–4029. (b) Lin, C.; Gitsov, I. *Macromolecules* **2010**, *43*, 3256–3267.
(25) Iván, B.; Haraszti, M.; Erdődi, G.; Scherble, J.; Thomann, R.; Mülhaupt, R. *Macromol. Symp.* **2005**, *227*, 265–273.
(26) Erdödi, G.; Janecska, Á.; Iván, B. *Wiley Polym. Networks Group Rev.* **1999**, *2*, 73–87.
(27) Bromberg, L.; Temchenko, M.; Hatton, T. A. *Langmuir* **2002**, *18*, 4944–4952.
(28) (a) Bruns, N.; Scherble, J.; Hartmann, L.; Thomann, R.; Iván, B.; Mülhaupt, R.; Tiller, J. C. *Macromolecules* **2005**, *38*, 2431. (b) Tobis, J.; Thomann, Y.; Tiller, J. C. *Polymer* **2010**, *51*, 35–45.
(29) (a) Bruns, N.; Tiller, J. C. *Macromolecules* **2006**, *39*, 4386–4394. (b) Hu, Z.; Chen, L.; Betts, D. E.; Pandya, A.; Hillmyer, M. A.; DeSimone, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 14244–14252. (c) Wang, Y.; Betts, D. E.; Finlay, J. A.; Brewer, L.; Callow, M. E.; Callow, J. A.; Wendt, D. E.; DeSimone, J. M. *Macromolecules* **2011**, *44*, 878–885.
(30) Bruns, N.; Tiller, J. C. *Nano Lett.* **2005**, *5*, 45–48.
(31) Iván, B.; Kennedy, J. P.; Mackey, P. W. U.S. Patent 5,0709,381, Dec 17, 1991.
(32) Lin, C.; Gitsov, I. *Macromolecules* **2010**, *43*, 10017–10030.
(33) Kennedy, J. P. *Macromol. Symp.* **2001**, *175*, 127–131.
(34) (a) Iván, B.; Kennedy, J. P.; Mackey, P. W. *ACS Symp. Ser.* **1991**, *469*, 194–202. (b) Iván, B.; Kennedy, J. P.; Mackey, P. W. *ACS Symp. Ser.* **1991**, *469*, 203–212. (c) Scherble, J.; Iván, B.; Mülhaupt, R. *Macromol. Chem. Phys.* **2002**, *203*, 1866–1871.
(35) Kennedy, J. P. *Macromol. Symp.* **1994**, *85*, 79–96.
(36) Haigh, R.; Fullwood, N.; Rimmer, S. *Biomaterials* **2002**, *23*, 3509–3516.
(37) (a) Rimmer, S.; German, M. J.; Maughan, J.; Sun, Y.; Fullwood, N.; Ebdon, J.; MacNeil, S. *Biomaterials* **2005**, *26*, 2219–2230. (b) Sun., Y.; Collett, J.; Fullwood, N. J.; Mac Neil, S.; Rimmer, S. *Biomaterials* **2007**, *28*, 661–670.
(38) Behraves, E.; Jo, S.; Zygourakis, K.; Mikos, A. G. *Biomacromolecules* **2002**, *3*, 374–381.
(39) Isayeva, I. S.; Gent, A. N.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2075–2084.
(40) (a) Künzler, J. F. *Trends Polym. Sci.* **1996**, *4*, 52–29. (b) Lai, Y. C.; Friends, G. D. *J. Biomed. Mater. Res.* **1997**, *35*, 349–356. (c) Xu, J. K.; Li, X. S.; Sun, F. Q. *Drug Delivery* **2011**, *18*, 150–158.
(41) Nicolson, P. C.; Vogt, J. *Biomaterials* **2001**, *22*, 3273–3283.
(42) (a) Du Prez, F.; Goethals, E. J.; Schue, R.; Qariouh, H.; Schue, F. *Polym. Int.* **1998**, *46*, 117–125. (b) Li, X.; Basko, M.; Du Prez, F.; Vankelekom, I. F. J. *J. Phys. Chem. B* **2008**, *112*, 16539–16545.
(43) Gudipati, C. S.; Finaly, J. A.; Callow, J. A.; Callow, M. E.; Wooley, K. L. *Langmuir* **2005**, *24*, 3044–3053.
(44) Hanko, M.; Bruns, N.; Tiller, J. C.; Heinze, J. *Anal. Chem.* **2006**, *78*, 6376–6383.
(45) (a) Guan, Y.; Zhang, W.; Wan, G.; Peng, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3812–3820. (b) Guan, Y.; Jiang, W.; Zhang, W.; Wan, G.; Peng, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *17*, 1784–1790. (c) Guan, Y.; Zhang, W.; Wan, G.; Peng, Y. *New J. Chem.* **2002**, *26*, 1682–1685. (d) Guan, Y.; Jiang, W.; Zhang, W.; Wan, G.; Peng, Y. *J. Appl. Polym. Sci.* **2002**, *85*, 351–357. (e) Guan, Y.; Ding, X.; Zhang, W.; Wan, G.; Peng, Y. *Macromol. Chem. Phys.* **2002**, *203*, 900–908.
(46) (a) Jonckheere, L.; Goethals, E.; Du Prez, F. E. *e-Polym.* **2003**, 064. (b) Lequieu, W.; Du Prez, F. E. *Polymer* **2004**, *45*, 749–757. (c) Adriaensens, P.; Strome, L.; Carleer, R.; Gelan, J. *Macromolecules* **2002**, *35*, 3965–3970. (d) Lequieu, W.; Van De Velde, P.; Du Prez, F.; Adriaensens, P.; Strome, L.; Gelan, J. *Polymer* **2004**, *45*, 7943–7951.
(47) Pol, B. J.; van Wachem, P. B.; van Luym, M. J.; van der Does, L.; Bantjes, A. *J. Biomed. Mater. Res.* **1996**, *32*, 307–320.
(48) Soykan, C.; Coskun, R.; Delibas, A. *J. Macromol. Sci., Pure Appl. Chem.* **2005**, *42*, 1603–1619.
(49) Radke, W.; Müller, A. H. E. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 583–594.
(50) Roos, S. G.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8331–8335.
(51) Kretz, M.; Meurer, B.; Lotz, B.; Weill, G. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 663–675.