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Temperature induced phase transition of interpenetrating polymer networks composed of poly(vinyl alcohol) and copolymers of *N*-isopropylacrylamide with acrylamide or 2-acrylamido-2-methylpropyl-sulfonic acid

András Szilágyi*, Miklós Zrínyi

Laboratory of Soft Matters, Department of Physical Chemistry, Hungarian Academy of Sciences,
Budapest University of Technology and Economics, Budapest 1521, Hungary

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Abstract

Interpenetrating polymer networks (IPNs) composed of poly(vinyl alcohol) (PVA) and poly(*N*-isopropylacrylamide-*co*-X) (PNIPAAm-*co*-X) were prepared by using a two-step method. Hydrophilicity of PNIPAAm chains was increased by adding acrylamide (AAm; hydrophilic neutral monomer) or 2-acrylamido-2-methylpropylsulfonic acid (AMPS; anionic charged monomer). The effect of the incorporation of chemically crosslinked PVA into the temperature induced phase transition as well as swelling behavior of the responsive hydrogels were studied. The volume phase transition (VPT) of IPNs was investigated by cloud point measurement and differential scanning calorimetry. Significant differences in volume phase transition enthalpies of PNIPAAm (ΔH_{VPT}) and volume phase transition temperatures (T_{VPT}) were found. The ΔH_{VPT} decreases with increasing co-monomer concentration. In several cases the phase transition was not followed by macroscopic shrinking of IPNs. Thus this property is advantageous for several technical applications.

Keywords: IPN; Collapse transition; ‘In situ’ two-step method

1. Introduction

In the past few decades there has been an increasing interest in hydrogels because no other class of materials than polymer gels can be made to respond to so many different stimuli. The stimuli that have been demonstrated to induce abrupt changes in physical properties are diverse, and include temperature, pH, solvent- or ionic-composition, electric field, light intensity as well as introduction of specific ions [1–4]. Because of their drastic change of properties in response to environmental stimuli, these hydrogels may be used in controlled drug delivery [5], molecular separation [6], tissue culture substrates [7] and several technical applications [8].

Crosslinked poly(*N*-isopropylacrylamide) (PNIPAAm) is a thermo-sensitive hydrogel which undergoes a volume phase transition (VPT) at its lower critical solution temperature (LCST) of around 34 °C. In water, below the volume phase transition temperature (T_{VPT}), PNIPAAm hydrogels are in a highly swollen state. Above the T_{VPT}, polymer chains collapse dramatically with a concurrent change in the related properties [9,10]. This thermally induced volume change is important and advantageous in several applications, like artificial muscles and drug delivery systems. However, this can be a strong drawback in some cases, such as smart ‘gel glasses’ [11,12]. Different strategies have been proposed to improve the response rate or swelling capacities of temperature sensitive hydrogels, but only a few articles report reduced size change of hydrogels with maintained related properties, e.g. optical characteristics [13].

Formation of interpenetrating polymer networks (IPNs) could be a possible solution. An interpenetrating polymer network IPN, is defined as a combination of two polymers in network form, at least one of which is synthesized and/or

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* Corresponding author. Tel.: +36 1 463 2119; fax: +36 1 463 3767.
E-mail address: aszilagyi@mail.bme.hu (A. Szilágyi).

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Table 1
Sample designations and feed compositions of PVA/P(NIPAAm-*co*-AAm) and PVA/P(NIPAAm-*co*-AMPS) IPNs in water

Sample designation	NIPAAm/AAm ($\mathrm{mmol\ kg^{-1}/mmol\ kg^{-1}}$)	Sample designation	NIPAAm/AMPS ($\mathrm{mmol\ kg^{-1}/mmol\ kg^{-1}}$)
AAm 0	750.0/0.0	AMPS 0	750.0/0.0
AAm 5	712.5/37.5	AMPS 1	742.5/7.5
AAm 10	675.0/75.0	AMPS 2	735.0/15.0
AAm 15	637.5/112.5	AMPS 3	727.5/22.5
AAm 20	600.0/150.0	AMPS 4	720.0/30.0
AAm 25	562.5/187.5	AMPS 6	705.0/45.0
AAm 30	525.0/225.0		

crosslinked in the immediate presence of the other. The interlocked structures of the crosslinked components are believed to ensure stability of the bulk and surface morphology [14]. In the present study we report the preparation of interpenetrating polymer networks made of poly(vinyl alcohol) and poly(*N*-isopropylacrylamide).

Shin et al. have studied the properties of semi-IPNs composed of PNIPAAm and various hydrophilic polymers, such as PVA [15]. In the presence of linear hydrophilic polymers, T_{VPT} shifted to a slightly lower temperature. This phenomenon was attributed to intermolecular interactions such as hydrogen bonding between PNIPAAm and hydrophilic polymers. Kim et al. have synthesized poly(vinyl alcohol) poly(*N*-isopropylacrylamide) interpenetrating networks. They studied the swelling kinetics [16], electroactive characteristics [17] and thermal properties [18] of their hydrogels. Thermal properties around the freezing point and above 200 °C were investigated intensively [19].

Swelling and mechanical properties are improved by formation of semi-IPNs or IPNs but usually the phase transition temperature of PNIPAAm is just weakly affected. It is important to adjust the T_{VPT}. This can be done in two ways: (1) By modify the chemical structure of the polymer network by copolymerization or (2) by using a mixture or solution, instead of water as a swelling agent. In general, the incorporation of hydrophobic comonomers leads to a lower T_{VPT} while hydrophilic and charged comonomers leads to a higher T_{VPT} [20–23].

In the present study we report the preparation of interpenetrating polymer networks composed of PVA and PNIPAAm-*co*-X by using a two-step method. NIPAAm was copolymerized with AAm or AMPS comonomers to adjust the VPT temperature. Temperature induced volume phase transition was characterized by cloud point measurements and differential scanning calorimetry (DSC). Swelling degree of the aforementioned IPNs was measured and a potential application is suggested.

2. Experimental

2.1. Materials

N-Isopropylacrylamide (NIPAAm) from Acros Organics was used as received. Analytical grade acrylamide (AAm), 2-acrylamido-2-methylpropylsulfonic acid (AMPS), *N*,*N*′-methylene-bisacrylamide (BAAm), poly(vinyl alcohol) (PVA, partially hydrolyzed, $M_{\mathrm{w}}=13{,}000$–$23{,}000$), 2-Oxo-pentanedioic acid (KGA) from Aldrich and glutaraldehyde (GDA) from Merck were used without further purification.

2.2. Preparation of IPNs

Syntheses of the PVA/P(NIPAAm-*co*-X) IPNs were performed in aqueous media according to the following ‘in situ’ two-step method. The prescribed amounts of the NIPAAm, comonomers of the NIPAAm, the cross-linking agents and the catalysts were added to a 15 wt% aqueous PVA solution. The pre-gel solution was diluted with distilled water to the final concentration of the PVA (10 wt%). The total concentrations of monomers of the second network were 750 $\mathrm{mmol\ kg^{-1}}$ in the mixture. Nitrogen gas was bubbled through the solution for 30 min prior to polymerization. The PVA chains were crosslinked by GDA at pH 2 at ambient temperature for 6 h in darkness. The PVA/GDA molar ratio in the hydrogels was 200:1. In the second step, PNIPAAm network was formed by a subsequent photo-crosslinking with 0.04 wt% KGA as a photo-initiator in the presence of BAAm. The P(NIPAAm-*co*-X)/BAAm molar ratio was 500:1. Photo-crosslinking was performed at 20 °C for 12 h. Gelation took place in Wassermann test-tubes of 8.7 mm diameter and 9.9 cm height. Table 1 shows the sample designations as well as the feed compositions for the PVA/P(NIPAAm-*co*-AAm) and PVA/P(NIPAAm-*co*-AMPS) IPNs.

2.3. Swelling experiments

After the preparation the cylindrical IPNs were carefully blotted in order to remove the excess solution on the surface and weighed. The gels were directly immersed in deionized water and swollen to equilibrium at various temperatures (ca 7 days). The relative swelling ratios (q_{r}) were calculated from the ratio of the swollen IPN weight to the initial weight of the IPN.

$$q_{\mathrm{r}}=\frac{m_{\mathrm{e}}}{m_0} \tag{1}$$

Table 2
Cloud point temperatures and characteristic values of DSC endothermic peaks of PVA/P(NIPAAm-*co*-X) IPNs in water

Sample designation	T_C (°C)	Minimum of the peak (°C)	FWHM (°C)	ΔH_{VPT} ($J\ g^{-1}{}_{PNIPAAm}$)
AAm 0	31.4 (0.2)	33.6 (0.1)	1.2 (0.1)	60.9 (3.9)
AAm 5	33.8 (0.9)	37.4 (0.1)	2.2 (0.1)	53.4 (2.1)
AAm 10	36.9 (0.9)	41.5 (0.1)	4.3 (0.1)	47.7 (2.9)
AAm 15	40.7 (1.0)	45.3 (0.1)	6.6 (0.2)	50.1 (1.4)
AAm 20	45.3 (1.0)	49.8 (0.2)	10.9 (0.5)	39.6 (1.9)
AAm 25	50.6 (1.2)	55.0 (0.3)	13.6 (1.7)	30.7 (2.7)
AAm 30	56.6 (1.0)	60.6 (0.8)	18.4 (2.1)	32.6 (0.9)
AMPS 0	31.4 (0.2)	33.6 (0.1)	1.2 (0.1)	60.9 (3.9)
AMPS 1	32.8 (0.5)	35.6 (1.4)	2.9 (0.2)	54.2 (2.8)
AMPS 2	36.1 (1.0)	38.8 (0.1)	5.3 (0.1)	54.5 (4.3)
AMPS 3	39.6 (0.2)	41.5 (0.2)	7.8 (0.2)	52.1 (3.9)
AMPS 4	43.6 (1.2)	45.2 (0.6)	12.9 (0.6)	44.8 (2.0)
AMPS 6	54.8 (3.4)	49.7 (1.0)	15.0 (1.0)	39.7 (3.1)

Numbers in parentheses represent standard deviations.

where m_e is the equilibrium swollen weight and m_0 the initial weight of the gel after the preparation.

2.4. DSC measurements

The microcalorimetric scans were performed by using a MicroDSCIII apparatus (SETARAM) operating at a scan rate of 0.50 °C min^{-1} in the temperature range of 10 up to 90 °C. The cooling process was also performed with the same scanning rate. About 100–200 mg swollen gel sample in an additional 500–600 μl of deionized water (distilled water purified with a Millipore Simplicity 185 filtration system) was kept at 10 °C for 1 h to obtain swelling equilibrium. For repeated cycles a 1 h delay at 10 °C was realized between the cycles. The temperatures at the minimum of the endotherms were referred to as the volume phase transition temperature (T_{VPT}) of IPNs.

2.5. Cloud point determination

The cloud point of gels was determined in a home made apparatus. Glass tubes containing the gel were immersed in a Haake P2-C30P thermostat. The temperature was gradually raised (0.2 K min^{-1}) and the transmitted light was recorded. The cloud point (T_C) was defined as the temperature belonging to the intersection of the baseline and the extrapolated straight line fitted to the response curve.

3. Results and discussion

Since AMPS contains sulfonic groups the swelling behavior of PVA/P(NIPAAm-*co*-AMPS) IPNs depends on pH. In order to avoid further problems, the pH of the system was kept at 5.6 and considered stable during the swelling experiments.

To determine the effect of AAm and AMPS comonomers on the volume phase transition temperature of the IPNs, DSC and cloud point measurements were performed. Since the DSC curves broaden at higher copolymer content, increasing the experimental error of the reading of the onset temperature, the minimum of the peak was used to characterize T_{VPT}. The shape of the peaks was characterized by their full width at half maximum (FWHM). The temperatures at the minimum of the DSC endotherms were referred to as the T_{VPT} of the IPNs and other characteristic values are summarized in Table 2.

Fig. 1 shows the DSC thermograms for PVA/P(NIPAAm-*co*-AAm) (1.a) and PVA/P(NIPAAm-*co*-AMPS) (1.b). A sharp and clear endotherm was observed in the case of PVA/P(NIPAAm). Its T_{VPT} is 33.6 °C, which is slightly lower than that of the T_{VPT} of pure PNIPAAm network 34.1 °C. These values are in good agreement with the literature data [15,24]. The ΔH_{VPT} of PVA/P(NIPAAm) IPN was found to be 60.9 J g^{-1} (6.89 kJ mol^{-1}), which is nearly the same as the heat of the phase separation of PNIPAAm polymer solution in water (6.3 kJ mol^{-1}[25]). The 6.89 kJ mol^{-1} is significantly larger than the value reported in literature for PNIPAAm networks [21,26]. The difference stems from the construction of our instrument and the traditional DSCs. The former allows bigger sample size and easier sample treatment. Both AAm and AMPS comonomers increase the T_{VPT} but there are differences

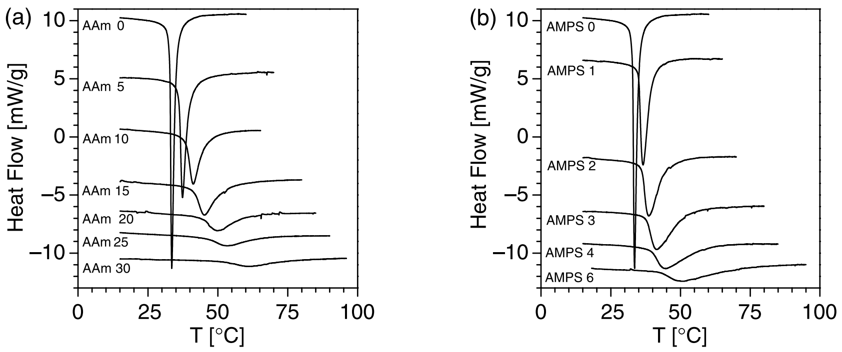

Fig. 1. Typical DSC thermograms at various copolymer compositions of PVA/P(NIPAAm-*co*-X) IPNs in water. Scanning rate was 0.5 °C min^{-1}. (a) X = AAm, (b) X = AMPS.

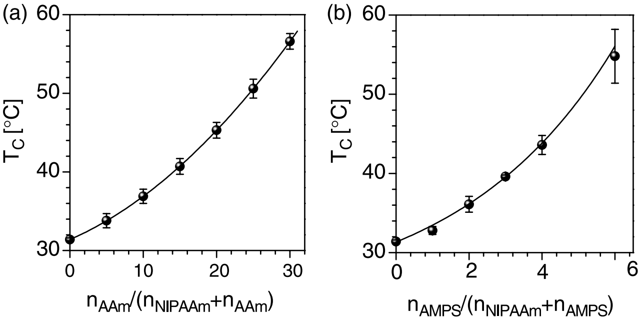

Fig. 2. Dependence of cloud point temperature (T_C) on comonomer content [mol%] of PVA/P(NIPAAm-*co*-X) IPNs in water. The heating rate was 0.2 °C min^{-1}. (a) X=AAm, (b) X=AMPS.

between the influence of non-ionic hydrophilic AAm and the charged AMPS. AMPS is more effective in increasing the T_{VPT}. It produces the same shift already at lower concentration (compare samples AAm 15 and AMPS 4). As the T_{VPT} increases, the endothermic DSC peaks broaden. This phenomenon is more pronounced in the PVA/P(NIPAAm-*co*-AMPS) IPNs. At high temperatures, the peaks almost disappear.

It is worth to mention that cooling and heating process do not provide the same T_{VPT}, a slight hysteresis occurs. However, we have found this hysteresis is typical for first order type phase transitions. Furthermore, the absolute values of the integrated heat flows were the same within the experimental accuracy at the heating and cooling process.

Optical properties also change when PVA/P(NIPAAm-*co*-X) IPNs undergo a VPT in water on increasing the temperature. However, the transparent–opaque transition temperature (T_C) is not identifiable as T_{VPT}. Fig. 2(a) shows the influence of copolymer composition on T_C of the PVA/P(NIPAAm-*co*-AAm) IPNs. In Fig. 2(b) T_C of the PVA/P(NIPAAm-*co*-AMPS) IPN is shown as a function of AAm content. The two T_C curves correlate relatively well with the VPT temperatures. The difference originates from the deviation of the two definitions and interpretation method.

According to the data in Table 2 the change in T_{VPT} is proportional to the comonomer content. Fig. 3 shows the ΔH of the phase transition of PVA/P(NIPAAm-*co*-X) IPNs as a function of T_{VPT}. As already observed in simpler PNIPAAm copolymer systems [20], a linear dependence was found.

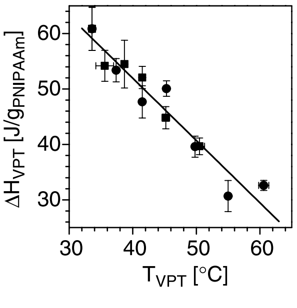

Fig. 3. Variation of the volume phase transition enthalpies (ΔH_{VPT}) as a function of T_{VPT} for PVA/P(NIPAAm-*co*-X) IPNs in water: (●) PVA/P(NIPAAm-*co*-AAm); (■) PVA/P(NIPAAm-*co*-AMPS).

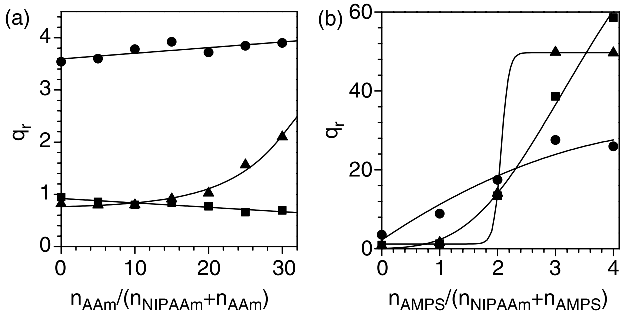

Fig. 4. The relative swelling ratio (q_r) as a function of X mol% in PVA/P(NIPAAm-*co*-X) IPNs at various temperatures: (●) 25 °C; (▲) 50 °C; (■) $T_{VPT}+10$ °C; (a) X=AAm, (b) X=AMPS.

Below the T_{VPT}, hydrophilic and hydrophobic parts of the PNIPAAm chain are hydrated by the water molecules. During the thermal induced volume phase transition, the structured water molecules around the hydrophobic isopropyl groups are released [27]. The water molecules around the hydrophilic parts of NIPAAm (and the hydrophilic comonomers) might not be influenced significantly. This is proved by the fact that the water content of the polymer network is relatively high after the phase transition, since the amide groups are still highly hydrated. Hydrophilic and charged comonomers of PNIPAAm probably modify only the T_{VPT} but do not directly influence the amount of water molecules around the isopropyl groups of PNIPAAm. Since the amount of water molecules surrounding the isopropyl groups of PNIPAAm depends on the temperature and not on the chemical characteristics of the copolymer chains, therefore, ΔH_{VPT} depends directly on the temperature at which the phase transition occurs. According to the microcalorimetric results, this dependence is linear function of T_{VPT}. This behavior is only weakly affected by the PVA network in spite of the ability of the PVA chains to establish hydrogen bonding.

The swelling degree of PVA hydrogels decreases with increasing swelling temperature (the so-called negative swelling behavior) [28]. However, we observed a weak positive swelling behavior on partially hydrolyzed PVA as a function of temperature. The negative swelling behavior of PNIPAAm is well documented [21]. Hydrogels prepared from AMPS or AAm show positive swelling behavior [3,8,23] and also affect the swelling degree of PVA/P(NIPAAm-*co*-X) IPNs.

In the Eq. (1) the relative swelling ratio (q_r) was defined as the ratio of the mass at equilibrium swelling to the mass of the sample after preparation. Fig. 4 shows the effect of copolymer composition on the relative swelling ratio at 25 and 50 °C for (a) PVA/P(NIPAAm-*co*-AAm) and (b) PVA/P(NIPAAm-*co*-AMPS) IPNs. An additional curve shows the q_r at 10 °C above the T_{VPT}. The relative swelling ratio of the pure PVA gel increases from 3.2 to 3.5 due to the 8.5 wt% PNIPAAm in the PVA gel at 25 °C and rises

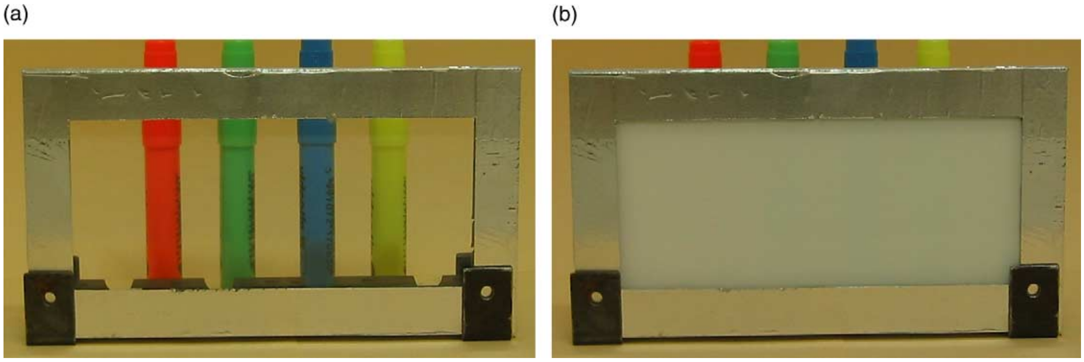

Fig. 5. The transparent–opaque transition of a gel-glass was made of PVA/PNIPAAm IPN ($T_C = 31.4$ °C).

continuously as the ratio of AAm increases in the network. As can be seen, PNIPAAm is rather hydrophilic below the T_{VPT} at 25 °C and AAm increases the hydrophilicity of PVA/P(NIPAAm-*co*-AAm) IPN. Above the T_{VPT}, the value of q_r of a PNIPAAm gel is around 0.1. The relative swelling ratio of PVA/P(NIPAAm-*co*-AAm) IPNs also decreases due to the collapse of P(NIPAAm-*co*-AAm) network. However, this decrease is not so significant as that of a pure PNIPAAm hydrogel and the value of q_r is around 0.85, which is important in the application detailed below.

AMPS drastically influences the relative swelling ratio of PVA/P(NIPAAm-*co*-X) IPNs below and above the T_{VPT}. At 25 °C, q_r changes from 3.5 to 26 as the ratio of AMPS is modified from 0 to 4 mol% in the P(NIPAAm-*co*-AMPS) network. The value of q_r of the PVA/P(NIPAAm-*co*-AMPS) IPNs is greater than 1, above the 1 mol% AMPS content. Above the T_{VPT}, the effect of AMPS is more significant, q_r changes from 0.9 to 58 in the examined interval. Positive swelling behavior of PAMPS dominates, in contrast to the negative swelling behavior of PNIPAAm.

On the basis of the responsive properties of the PVA/P(NIPAAm-*co*-X) IPNs, a window was fabricated. A PVA/P(NIPAAm-*co*-X) IPN layer was placed between two glass sheets (Fig. 5). The so-called 'gel-glass' becomes opaque when its temperature exceeds a critical value and goes back to its original transparent state when it is cooled below this temperature. This window is able to control the sunlight or heat radiation. Fig. 5(a) shows the window at ambient temperature, where the 'gel-glass' is completely transparent, as is illustrated by the colour markers behind the window. Above the critical temperature the 'gel-glass' becomes fully opaque, as shown in Fig. 5(b).

4. Conclusion

Temperature sensitive PVA/P(NIPAAm-*co*-X) IPNs were prepared by an 'in situ' two-step method. The volume phase transition temperature of IPNs was shifted to higher temperatures due to the hydrophilic neutral or anionic comonomers of NIPAAm. MicroDSC study results indicate that the enthalpy of the volume phase transition does not depend on the chemical composition but rather on the temperature at which the volume phase transition occurs. The influence of the PVA network on T_{VPT} of the P(NIPAAm-*co*-X) is negligible. Studies of the swelling properties show that in several cases the VPT of these IPNs was not followed by macroscopic shrinking and that these preparations are suitable for manufacturing 'gel-glasses'.

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