Phase Transitions in Pure and Hybrid Hydrogels: A Fluorescence Study

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Summary: Recent observations on phase transitions around the critical point showed that the critical exponents differed drastically from percolation results and classical results for pure hydrogel systems, depending on monomer concentration. In addition to pure hydrogels, the sol-gel phase transition during radical crosslinking copolymerization of acrylamide (AAm) and *N*-isopropylacrylamide (NIPA) hybrid was studied by using the *steady state* fluorescence (SSF) technique. *N,N′*-methylenebis(acrylamide) (BIS) and ammonium persulfate (APS) were used as crosslinker and initiator, respectively. Pyranine (trisodium 8-hydroxypyrene-1,3,6-trisulfonate acid, HPTS) was added as a fluoroprobe for monitoring the polymerization. It was observed that pyranine binds to AAm and NIPA chains on the initiation of the polymerization, thus the fluorescence spectra of the bonded pyranines shift to shorter wavelengths. Fluorescence spectra of the bonded pyranines allowed to monitor the sol-gel phase transition without disturbing the system mechanically and to test the universality of the sol-gel transition as a function of polymer concentration ratios. The observations around the gel point of PAAm-PNIPA hybrid show that the gel fraction exponent β obeyed the percolation result.

Keywords: critical phenomena; fluorescence; hybrid; hydrogels; percolation

Introduction

Hydrogels are important materials for both fundamental and technological reasons.[1] It is well known that the PNIPA hydrogel in an aqueous solution exhibits a rapid and reversible hydration–dehydration change in response to small temperature changes around its lower critical solution temperature (LCST). Below this temperature the hydrogel is swollen, hydrated and hydrophilic, whereas above the LCST, the hydrogel shrinks and forms a collapsed, dehydrated and hydrophobic state due to the breakdown of the delicate hydrophilic/hydrophobic balance in the network structure. Poly(*N*-isopropylacrylamide) (PNIPA) gel is a temperature-sensitive gel exhibiting volume phase transition at approximately 34 °C.[2,3] The temperature sensitivity of PNIPA gels has been studied both for its fundamental interest and technological application.[4–7] These materials are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators. On the other hand, polyacrylamide gel, an example of hydrogels, is a potent water-absorbent, forming a soft gel used in applications such as polyacrylamide gel electrophoresis and in manufacture of soft contact lenses. In the straight-chain form, it is also used as a thickener and suspension agent. More recently, it has been used as subdermal filler for aesthetic facial surgery.

Hydrogels have received considerable attention due to the sol-gel phase transition process. Even though the sol-gel phase transition is not a phase transition in thermodynamic sense, but rather a geometrical one, as a subject of critical phenomena,

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it behaves like a second-order phase transition constituting a universal class by itself. The exact solution of the sol-gel phase transition was first given by Flory and Stockmayer[8,9] on a Bethe lattice on which the closed loops were ignored. An alternative to the chemical-kinetic theory is the lattice percolation model[10,11] where monomers are assumed to occupy the sites of a periodic lattice. A bond between these lattice sites is formed randomly with probability p. For a certain bond concentration p_c, defined as the percolation threshold, the infinite cluster starts to form in the thermodynamic limits. This is called the percolation cluster in polymer language. The polymeric system is in the sol state below the percolation threshold, p_c.

In this work, we would like to compare the radical crosslinking copolymerization of AAm-NIPA hybrids[12] with the neat AAm and NIPA hydrogel systems. Here the total monomer concentration for the hybrids is kept at 2 M. Very small amounts of pyranine added to the pre-polymerization solution led to a spectral shift to shorter wavelengths upon the initiation of polymerization. This spectral shift is due to the binding of pyranine to polymer chains during the AAm-NIPA polymerization. Pyranine, thus, becomes an intrinsic fluoroprobe while it is extrinsic at the beginning of the reaction. The fluorescence intensity of the pyranine bonded to polymer chains allows directly to measure the gel fraction near the sol-gel phase transition, and thus the corresponding critical exponent, β.

Experimental Part

Hybrids were prepared from various amounts of AAm (Merck) and NIPA (Merck) monomers. The monomer concentrations, gel points, critical amplitudes C^+, C^- and critical exponents β are given in Table 1. BIS (Merck) was dissolved in $25 \times 10^{-6} \, \text{m}^3$ of water to which 10^{-4} l of TEMED (tetramethylethanenediamine) was added as an accelerator. The initiator, ammonium persulfate (APS, Merck), was

Table 1.
Parameters of AAm-NIPA hybrid gels.

AAm [M]	BIS [M]	NIPA [M]	t_c (s)	C^-/C^+	β
2.0	0.013	0	300 ± 5	1.00	0.92
				0.37	0.50
				0.28	0.55
				0.23	0.52
				0.10	0.52
1.8	0.013	0.2	300 ± 5	1.00	0.85
				0.37	0.52
				0.28	0.55
				0.23	0.55
				0.10	0.46
1.6	0.013	0.4	420 ± 5	1.00	0.75
				0.37	0.63
				0.28	0.66
				0.23	0.65
				0.10	0.70
1.5	0.013	0.5	480 ± 5	1.00	1.06
				0.37	0.63
				0.28	0.60
				0.23	0.61
				0.10	0.56
1	0.013	1	600 ± 5	1.00	0.95
				0.37	0.58
				0.28	0.57
				0.23	0.55
				0.10	0.44
0.5	0.013	1.5	1080 ± 5	1.00	0.88
				0.37	0.40
				0.28	0.32
				0.23	0.33
				0.10	0.34
0.4	0.013	1.6	1500 ± 5	1.00	0.87
				0.37	0.37
				0.28	0.37
				0.23	0.31
				0.10	0.31
0.2	0.013	1.8	1800 ± 5	1.00	0.86
				0.37	0.45
				0.28	0.36
				0.23	0.32
				0.10	0.33
0	0.013	2.0	–	1.00	opaque
				0.37	
				0.28	
				0.23	
				0.10	

recrystallized twice from methanol. The initiator and pyranine concentrations were kept constant at 7×10^{-3} M and 4×10^{-4} M, respectively, for all experiments. All samples were deoxygenated by bubbling nitrogen for 10 min, just before the polymerization started.

The fluorescence intensity measurements were carried out using a Model LS-50 spectrometer of Perkin-Elmer, equipped with temperature controller. All

measurements were made at the 90° position and slit widths at 5 nm. Pyranine was excited at 340 nm in *in situ* gelation experiments. Changes in the fluorescence spectra and emission intensity of pyranine were monitored as a function of polymerization time.

Results and Discussion

Our recent observations around the critical point showed that the critical exponents did not obey the same universality class for neat AAm[13] and NIPA[14] hydrogels, while bulk gels[15–18] were modeled by percolation picture. In neat AAm hydrogels, it was shown that the critical exponents agree best with the percolation results for higher AAm concentrations above 1 M, but they crossover from percolation to classical (mean-field or Flory-Stockmayer) values when the AAm concentration goes from 2 M down to 1 M, and the present classical values below 1 M. Further down below 0.5 M, however, no gelation was observed.[13] The gel fraction (above the gel point) and average cluster size (below the gel point) exponents and the gel points (for 1 M PAAm hydrogel for various BIS contents) are summarized in Table 2.

On the other hand, in NIPA hydrogels[14] the monomer concentration was chosen as 1 M to prevent the system from opacity for various crosslinker contents and the produced gel fraction and average cluster size (both above the gel point) exponents were found to agree with the classical results. Here a decrease in the average cluster size of the finite clusters above the gel point is measured by scattered light measurements. The critical exponents and the gel points (for 1 M NIPA hydrogel and various BIS contents) are summarized in Table 3. Here BIS contents were kept lower to avoid opacity.

Hybrid hydrogels were studied to investigate the behavior of critical exponents. Our aromatic probe pyranine is a highly water-soluble compound with well characterized photophysical properties.[19]

Table 2.
Parameters of 1 M PAAm hydrogels for various BIS contents.

AAm [M]	BIS [M]	t_c (s)	C^-/C^+	β	γ
1.0	0.013	222 ± 5	1.00	1.00 ± 0.02	0.80 ± 0.05
			0.37	1.20 ± 0.02	
			0.28	1.20 ± 0.02	
			0.23	1.20 ± 0.02	
			0.10	1.14 ± 0.02	
1.0	0.019	185 ± 5	1.00	1.02 ± 0.02	1.00 ± 0.05
			0.37	1.20 ± 0.02	
			0.28	1.20 ± 0.02	
			0.23	1.17 ± 0.02	
			0.10	1.15 ± 0.02	
1.0	0.026	195 ± 5	1.00	1.01 ± 0.02	0.80 ± 0.05
			0.37	1.17 ± 0.02	
			0.28	1.17 ± 0.02	
			0.23	1.10 ± 0.02	
			0.10	1.19 ± 0.02	
1.0	0.032	163 ± 5	1.00	1.00 ± 0.02	0.90 ± 0.05
			0.37	1.40 ± 0.02	
			0.28	1.40 ± 0.02	
			0.23	1.40 ± 0.02	
			0.10	1.20 ± 0.02	

Figure 1 shows the typical fluorescence spectra of pyranine at different stages of the AAm-NIPA copolymerization. It can be observed that, at the beginning of the reaction, only the 508 nm peak exists, then the intensity of the new peak (short-wavelength, around 380 nm) started to increase and shift from 380 to 427 nm as the intensity of the 508 nm peak (long-wavelength peak) decreased in the hybrid system. The shifts in the emission spectra of pyranine during the polymerization[13] give more information about the microscopic nature of the polymer-probe interaction as was already described in our previous study.[20] In that study, we proved that the probability of bonding pyranine to the system over more than one functional

Table 3.
Parameters of 1 M NIPA hydrogels for various BIS contents.

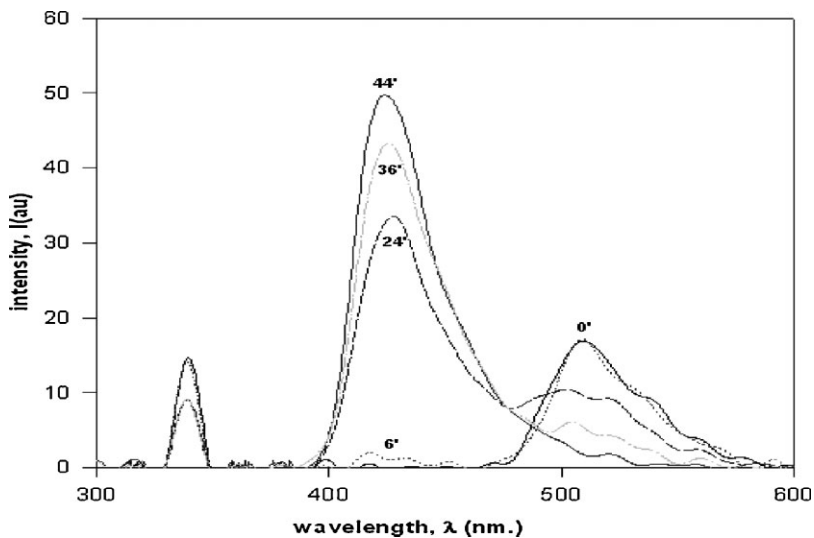| NIPA [M]	BIS [M] (×10⁻²)	T (°C)	t_c (s)	β	γ'
1	0.648	21	720 ± 5	0.8	1.0
1	1.038	21	720 ± 5	1.10	0.9
1	1.298	21	660 ± 5	1.25	0.8
1	1.558	21	600 ± 5	1.12	0.9
1	1.882	21	480 ± 5	0.9	0.9

Figure 1.

Typical fluorescence spectra of pyranine at different stages of AAm-NIPA polymerization. The numbers show the corresponding reaction times (min).

group may increase with increasing polymer concentration and also with the reaction time. As the polymerization progresses pyranine can have a chance to bind the polymeric system over two or three functional groups. Here a considerable shift from 508 to 380 nm occurs, as previously observed,[20,21] in the emission spectra when the OH group in pyranine binds covalently to the vinyl group of the growing AAm and NIPA polymer chains. At the same time, the shift in the short-wavelength peak between 380 and 427 nm is due to electrostatic binding of SO_3^- groups on pyranine to the AAm and/or NIPA monomers with protonated amide groups, whether on the same polymer molecule or on the other polymer chains. In other words, we observed a considerable blueshift, from 508 nm to 380 nm in the emission spectra due to a $C-O$ ether bond formation between the OH oxygen of 3s PyOH and the terminal C-atom of the growing AAm chain. Furthermore, ionic (electrostatic) interactions occur between the three ionized sulfonic acid groups (SO_3^-) of 3s PyOH and protonated amide groups on the AAm chains. These electrostatic interactions cause a gradual red shift in the maximum of the short-wavelength peak, from 380 to 427 nm. The results showed that pyranine can be used as a probe for real-time monitoring of polymerization of the AAm system since it monitors both the progress of the polymerization via chemical binding using OH group and the change in the local density of the polymerizing sample by means of the gradual red shift in the short-wavelength-peak via ionic interactions over SO_3^- groups.[20]

Figure 2a–c present the fluorescence intensity of the 512 nm peak, I_{512} (corresponding to free pyranine in the sample cell) for the neat AAm, neat NIPA and their hybrids, respectively. Here neat AAm and neat NIPA are added for comparison. As seen in Figure 2a, the fluorescence intensity of free pyranine, for neat AAm gelation, first increased then decreased down to some point, and then decreased to zero at the end of the reaction. On the other hand, for neat NIPA gelation (Figure 2b) and in the mixed systems (Figure 2c), the fluorescence intensity of free pyranine first decreased then increased up to some point again, but then did not decrease to zero at the end of the reaction. It is seen from the figure, there are some
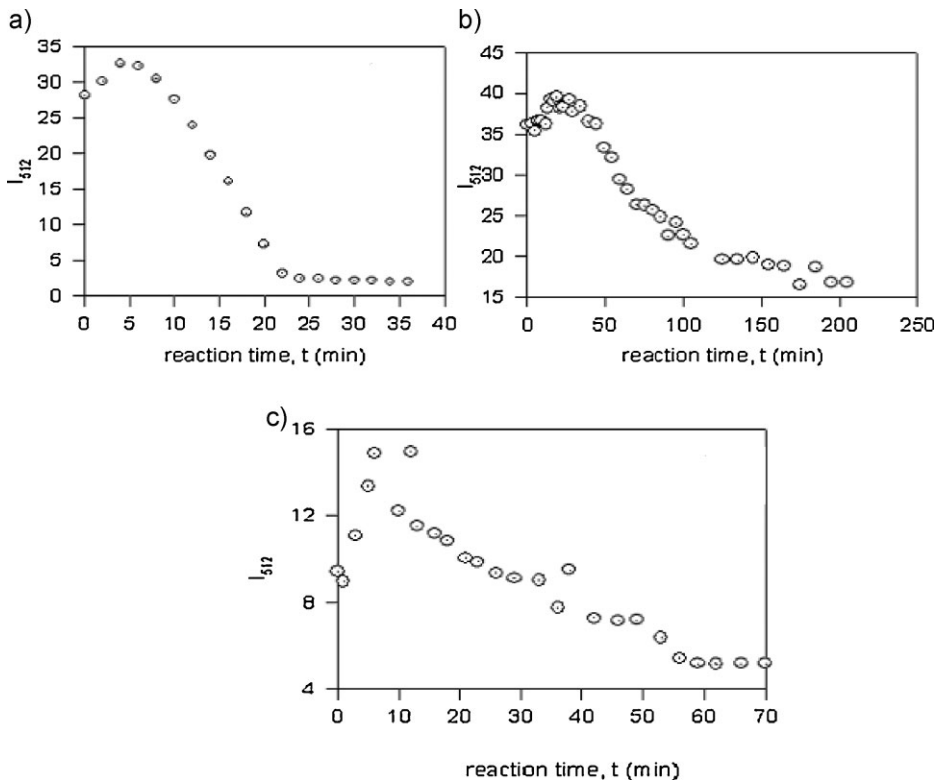
a)

b)

c)

Figure 2.
Fluorescence intensity of free pyranine at 512 nm, I_{512}, versus reaction time for (a) 100%AAm, (b) 100% NIPA and (c) 50%AAm-50%NIPA concentrations.

unreacted monomers at the end of the reaction depending on the NIPA content. It is also indicated (Figure 2a and 2b) that neat NIPA gelation takes a longer time than neat AAm gelation.

Figure 3a–c compare the fluorescence intensities from the bonded pyranine versus the reaction time for neat AAm, neat NIPA and their hybrids, respectively. This is observed here for all systems, since the maxima of the spectra, I_{max}, (corresponding to bonded pyranine) shift from 380 to 427 nm, due to (electrostatic) interactions occurring between the three ionized sulfonic acid groups (SO_3^-) of 3s PyOH and protonated amide groups in the AAm chains. As the polymerization progresses, there is no chance of monitoring the intensity in the time drive mode of the spectrometer (10 possible data in 1 s). Therefore, we monitored the fluorescence

spectra in relatively long periods of time and plotted the intensity I_{max} corresponding to the maxima of the spectra as a function of time. We, then, used these data to evaluate the critical behavior of the sol-gel phase transition.

In order to determine the gel points, t_c, each experiment was repeated at the same experimental conditions, and the gel points were determined by dilatometric technique.[22] A steel sphere of 4.8 mm diameter was slowly moved in the sample up and down by means of a piece of magnet applied on the outer face of the sample cell. The time at which the movement of the sphere stops was considered as the onset of the gel point, t_c. The t_c values for hybrid system are summarized in Table 1 together with the other parameters.

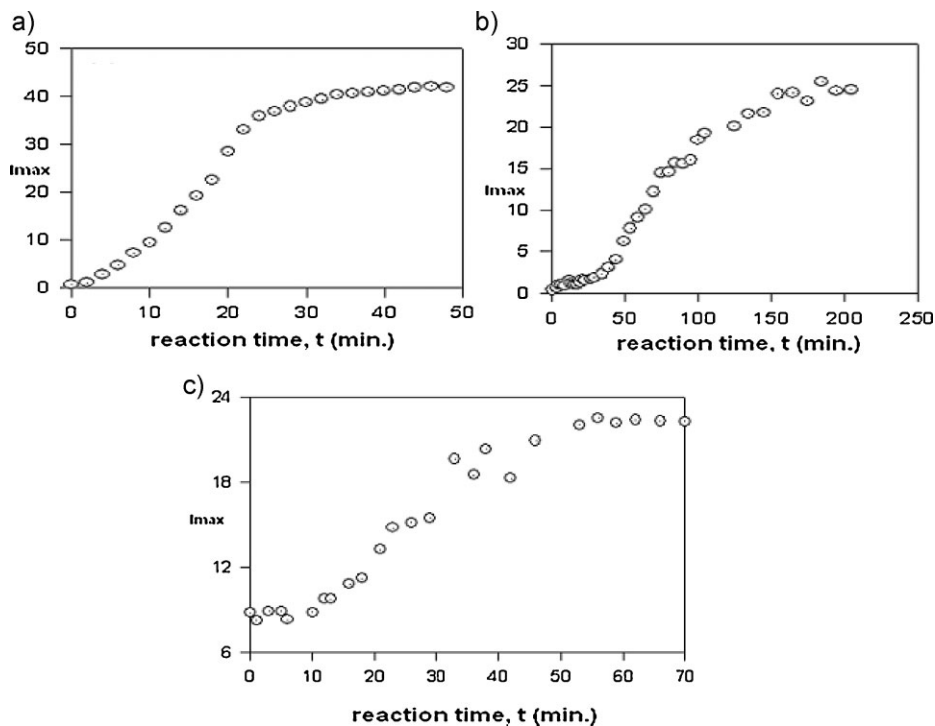Here, one would like to argue that the total fluorescence intensity from the bonded

Figure 3.
Fluorescence intensity variation of pyranine bonded to the gel for (a) 100% AAm, (b) 100% NIPA and (c) 50% AAm-50% NIPA concentrations, versus reaction time.

pyranine monitors the weight-average degree of polymerization and the growing gel fraction below and above the gel point. Therefore, below the gel point, i.e., for $t < t_c$, the maximum fluorescence intensity, I_{max}, measures the weight average degree of polymers (or average cluster size). Above t_c, if the intensity from finite clusters distributed through the infinite network I_{ct} is subtracted from the maximum fluorescence intensity, then, the corrected intensity $I_{max}-I_{ct}$ measures solely the gel fraction G, the fraction of the monomers that belong to the macroscopic network. In summary, we have the following relations,

$$I_{max} \propto DP_w = C^+(t_c - t)^{-\gamma}, \quad t \to t_c^- \quad (1a)$$

$$I_{ct} \propto DP_w = C^-(t_c - t)^{-\gamma'}, \quad t \to t_c^+ \quad (1b)$$

$$I_{max} - I_{ct} \propto G = B(t - t_c)^{\beta}, \quad t \to t_c^+ \quad (2)$$

where C^+, C^- and B are the critical amplitudes.

The gelation theory often makes the assumption that the conversion factor, p, alone determines the behavior of the gelation process, though p may depend on temperature, concentration of monomers, and time.[10,11] If the temperature and concentration are kept fixed, then p is directly proportional to the reaction time, t. This proportionality is not linear over the whole range of reaction time, but it can be assumed that in the critical region, i.e. around the critical point $|p - p_c|$ is linearly proportional to the $|t - t_c|$.[23,24]

It is well known that the average cluster size of the finite clusters (distributed through the infinite network) above the gel point decreases with the same, but negative slope of the increasing cluster size before the gel point. This means that the exponents γ and γ', defined for the cluster sizes below and above the gel point, have the same values.[10,11,25,26] But, the critical amplitudes for the average cluster size

Table 4.
The estimated values for the ratio C^-/C^+ (ref.[27]).

|	Classical	Percolation			
		Direct ε expansion	$\gamma_{\varepsilon exp} = 1.840$ and $\beta_{\varepsilon exp} = 0.52$	$\gamma = 1.7$ and $\beta = 0.4$	Series and MonteCarlo
C^-/C^+	1	0.37	0.28	0.23	0.1

defined below (C^+ in Equation 1a) and above (C^- in Equation 1b) the gel point are different, and there exists a universal value for the ratio C^+/C^-. This ratio is different for mean-field versus percolation as discussed by Aharony[27] and Stauffer.[10] The estimated values for $C^-/C^{+[10,27]}$ are given in Table 4.

It is clarified in Figure 4 that to determine the intensity I_{ct} in Equation 1b and 2, we first choose the parts of the intensity-time curves up to the gel points, then the mirror symmetry I_{ms} of these parts according to the axis perpendicular to time axis at the gel point were multiplied by the ratio C^-/C^+, so that $Ict = \frac{C^-}{C^+}I_{ms}$. Thus, I_{ct} measures solely the intensity from the cluster above the gel point, and $I_{max} - I_{ct}$ measures the intensity from the gel fraction.

Using the Equation 1 and 2, and the values for t_c summarized in Table 1–3, we calculated β exponents as a function of monomer concentration. Figure 5a and b represent the log-log plots of the typical intensity-time data above the gel point, for 25% and 50% NIPA concentrations ($C^-/C^+ = 0.28$), respectively, where the slopes of the straight lines close to the gel points give β exponents. The obtained β values are listed in Table 1 for various monomer contents. On the other hand, γ exponents did not obey any scaling behavior.[14] Here we have to note that β exponents as seen in Table 1 strongly support that the AAm-NIPA hybrid during gelation obeys the percolation picture.

On the other hand, AAm-NIPA gel samples were annealed at 21 °C to 80 °C to investigate the temperature dependence of fluorescence emission and scattered light intensities. It is observed that fluorescence emission intensity for neat 2 M AAm gel decreases when the temperature increases from 21 °C to 80 °C. For 100% (2 M) AAm gel, the fluorescence intensity decreases since non-radiative transition increases. Then AAm concentration decreased and NIPA concentration gradually increased. It
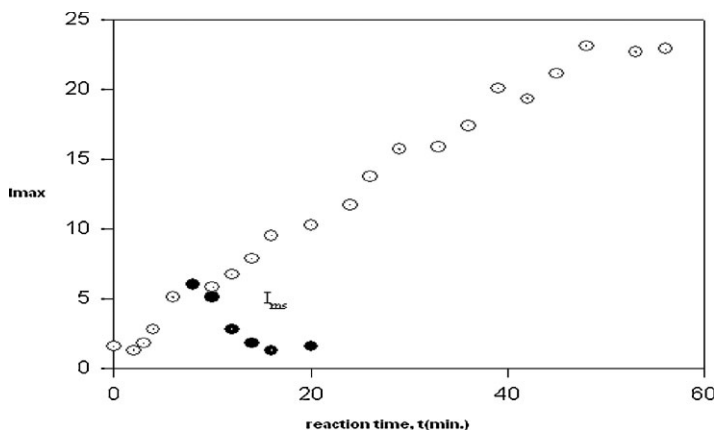
Figure 4.
Flourescence intensity-time curve during polymerization of AAm. The curve depicted by dots represents the mirror symmetry I_{ms} of the intensity according to the axis perpendicular to time axis at $t = t_c$. The intensity from the clusters above the gel point is calculated as $I_{ct} = \frac{C^-}{C^+}I_{ms}$. Thus, $I_{max} - I_{ct}$ monitors the growing gel fraction for $t > t_c$. The intensity from the low part of the symmetry axis monitors the average cluster size for $t < t_c$.
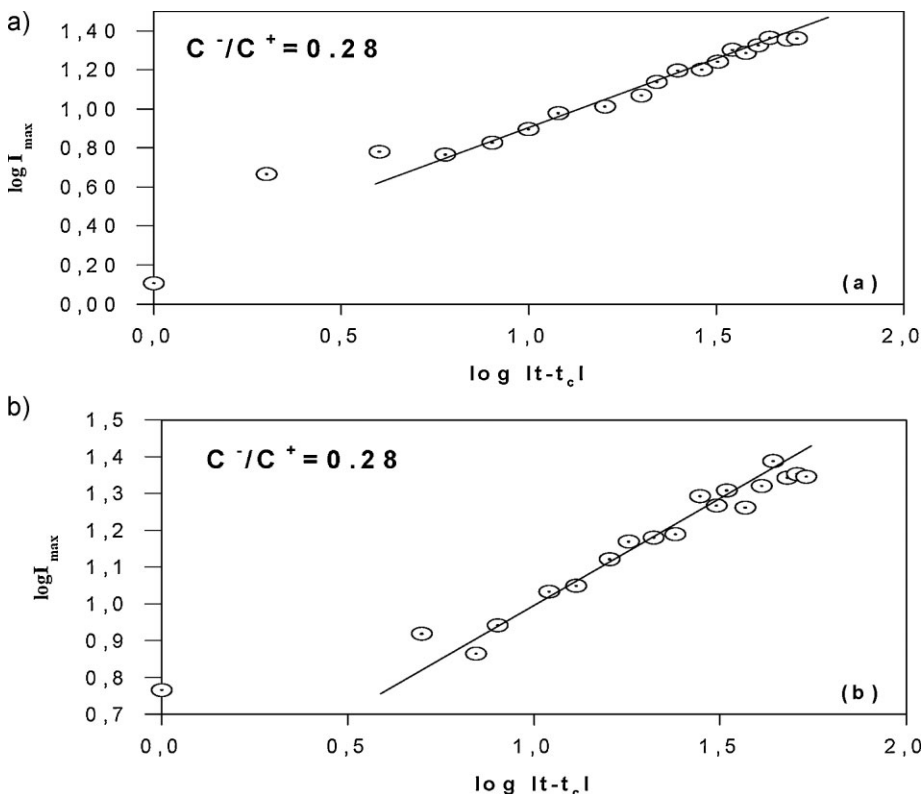
Figure 5.
Double logarithmic plot of the intensity $I_{max}-I_{ct}$ versus time curves above t_c for (a) 25% NIPA and (b) 50%NIPA concentration, (where $C^-/C^+ = 0.28$). The β exponents were determined from the slope of the straight lines.

is known that linear PNIPA exhibits a lower critical solution temperature (LCST) of 34 °C and its crosslinked gel undergoes temperature-induced phase transitions at this temperature.[2]

Below LCST, PNIPA is hydrophilic and possesses individual random coils in water, while at higher temperatures, PNIPA becomes hydrophobic. For lower NIPA contents (10 and 20%), the LCST of the mixture gel system is about 45 °C. When we increased NIPA concentration to 50%, the LCST value of the hybrid gel system decreases to 40 °C. Above 75% NIPA, LCST is around 35 °C and so it reaches the LCST for AAm-NIPA hybrid gels. The temperature dependence of the fluorescence intensity for a chosen higher AAm and NIPA contents are shown in Figure 6. The LCST values for various NIPA concentrations are given in Table 5. The main

result is that as the NIPA content in the mixture decreased, the LCST of the NIPA shifted to higher temperature. When we increased the NIPA content in the mixture, it reached its LCST near 35 °C.

In conclusion this work has presented a study of the radical crosslinking copolymerization of AAm-NIPA hybrid systems where the critical exponents were determined in the view of universality. It was observed that, in neat AAm hydrogels, the critical exponents differ from classical values, the percolation values depending on monomer concentration. For higher AAm concentration (2–5 M) the exponents are in accord with percolation results, while for lower AAm concentration (0.5–1 M) the exponents obey classical results.[13] On the other hand, in neat 1 M NIPA hydrogels[14] the critical exponents are in good agreement with classical results. In the present
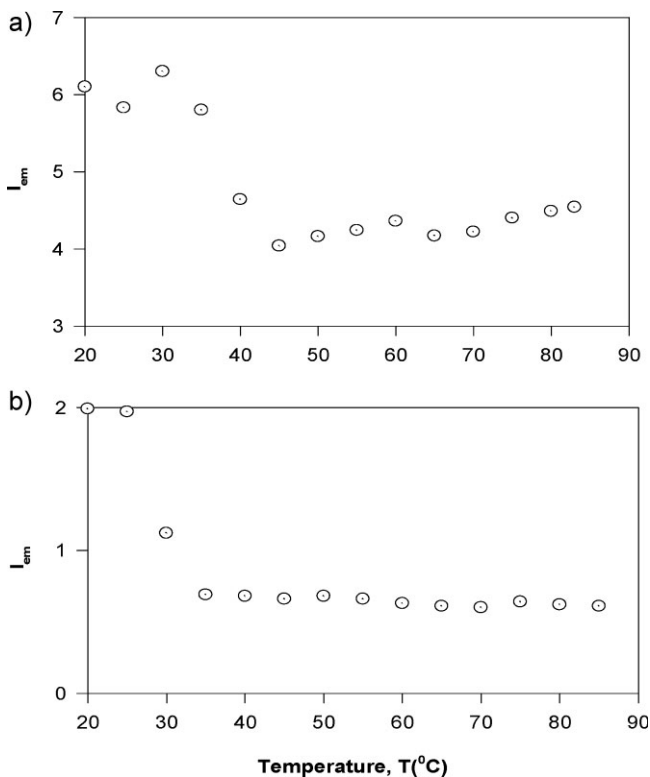
Figure 6.
Temperature dependence of fluorescence intensity for (a) higher AAm concentration and (b) higher NIPA concentration.

Table 5.
Parameters for hybrids of AAm-NIPA.

AAm [M]	BIS [M]	NIPA [M]	T (°C)
2.0 (100%)	0.013	0 (0%)	–
1.8 (90%)	0.013	0.2 (10%)	45
1.6 (80%)	0.013	0.4 (20%)	45
1.5 (75%)	0.013	0.5 (25%)	42
1.0 (50%)	0.013	1.0 (50%)	40
0.5 (25%)	0.013	1.5 (75%)	35
0.4 (20%)	0.013	1.6 (80%)	35
0.2 (10%)	0.013	1.8 (90%)	35
0 (0%)	0.013	2.0 (100%)	opaque

work, the critical exponents of AAm-NIPA hybrid hydrogels were investigated for various monomer concentrations. It was observed that the gel fraction exponent β agrees best with the percolation theory for various amounts of PAAm-NIPA hybrid.[12] We were thus able to measure the copolymerization kinetics obeying the percolation picture without disturbing the system mechanically. In the meantime

the universality of the sol-gel transition was tested as a function of parameters like polymer concentration ratios. Here, we have to mention that the percolation depends on monomer concentration, differing much from the bulk systems,[15–18] where the glassy regions percolate. The other most interesting result of this work is that the LCST varies as a function of the NIPA content of the AAm-NIPA hybrid gel system.

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