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Inhomogeneities in poly(acrylamide) gels: position-dependent elastic modulus measurements

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Summary

The inhomogeneities in poly(acrylamide) (PAAm) gels and the formation mechanism of inhomogeneities were investigated using the results obtained by the mechanical measurements. The gels in the form of rods of 5.6 mm in diameter were prepared at various crosslinker (N,N'-methylene(bis)acrylamide) content. The initial monomer concentration was set to 5.1 w/v %. The results show that the elastic modulus of PAAm gels varies depending on the location, at which the mechanical measurements are carried out. The modulus increases with increasing distance from the bottom of the gel rod. The extent of modulus variation along the gel increases with increasing crosslinker content from 2.6 to 9 % BAAm.

Introduction

Polyacrylamide (PAAm) gels are usually prepared by free-radical crosslinking copolymerization of acrylamide (AAm) and N,N'-methylene(bis)acrylamide (BAAm) monomers. Previous studies show that the physical properties of PAAm gels such as the equilibrium degree of swelling, elastic modulus, and the clarity strongly depend on the conditions of the gel preparation, i.e., on the initial monomer concentration and on the crosslinker (BAAm) content [1-17]. Experiments also show formation of opaque PAAm gels above a critical crosslinker concentration [9]. The opacity in gels is known to be due to the spinodal decomposition of the polymer network concentration into smaller domains with two different densities, one dilute and the other dense. These concentration fluctuations can scatter light and reduce the transmission of visible light through the gel. Domain formation in polymer gels and resulting inhomogeneities and heterogeneities are usual features of polymer networks produced by free-radical polymerization reactions. This is due to the fact that the formation of a network chain by free-radical mechanism takes place within a short period of time (usually less than one second) compared to the relatively long relaxation times of the network chains. Thus, the concentration fluctuations are "frozen" in the final network. Note that, although there has been some diversity in defining the inhomogeneity and heterogeneity in gels, inhomogeneity usually means the fluctuations of the crosslink density in space whereas heterogeneity indicates the existence of phase separated domains in polymer gels. Network inhomogeneities have been studied using light scattering techniques for various neutral or polyelectrolyte gels [6,18,19]. The results indicate increasing extent of inhomogeneities in gels with increasing crosslinker concentration.

In this report, we will discuss the inhomogeneities in PAAm gels and the formation mechanism of inhomogeneities using the results obtained by the mechanical measurements. In our preliminary experiments, we observed that the elastic modulus of some PAAm gels varies depending on the location, at which the mechanical measurements are carried out. The position dependent elastic modulus in gels has, to our knowledge, not been reported before. We prepared a series of PAAm gels in the form of rods at various crosslinker (BAAm) content. From each gel rod, samples were taken from different locations and subjected to mechanical measurements. The variation of the elastic modulus depending on the location of the measurement was studied at various crosslinker contents. As will be shown below, the development of gel inhomogeneities can be monitored from the extent of the variation of the elastic modulus along the gel sample.

Experimental

Synthesis of Hydrogels

AAm (Merck) was crystallized from acetone / ethanol mixture (70/30 by volume) below 30°C. BAAm (Merck) and potassium persulfate (KPS, Merck) were used as received. BAAm stock solution was prepared by dissolving 0.3285 g of BAAm in 25 mL of distilled water. KPS stock solution was prepared by dissolving 0.1 g of KPS in 25 mL of distilled water. Distilled and deionized water was used for the swelling experiments. For the preparation of the stock solutions and for the hydrogel synthesis, distilled and deionized water was distilled again prior to use and cooled under nitrogen bubbling.

The crosslinking copolymerization was carried out in water, as the polymerization solvent, at 40°C in the presence of 0.474 mM KPS as the initiator. The total monomer concentration was fixed at 5.1 w/v %, while the crosslinker (BAAm) content was varied between 2.6 and 20.6 wt% (with respect to the monomers). To illustrate the synthetic procedure, we give details for the preparation of the hydrogel with 2.6 wt % BAAm in the comonomer feed composition:

AAm (0.497 g), stock solutions of BAAm, and KPS (1 mL and 0.32 mL, respectively), were dissolved in 8.68 mL of distilled water. After bubbling nitrogen for 20 min, the solution was poured into several glass tubes of 5.6 mm internal diameters and about 100 mm long. Thereafter, 10 min of nitrogen bubbling was required through each solution to obtain reproducible results. The glass tubes were sealed, immersed in a thermostated water bath at 40°C and the polymerization was conducted for one day. Both the gel fraction and the monomer conversion measurements [20] showed that all the gel formation reactions were complete after one day of crosslinking copolymerization.

Swelling measurements in water

The hydrogels were freed from the tubes and they were cut into samples of about 7 mm length. Then, each sample was placed in an excess of water at room temperature

(19 ± 1°C). In order to reach the equilibrium degree of swelling, the hydrogels were immersed in water for at least two weeks during which water was replaced every other day; the swelling equilibrium was tested by measuring their diameters. The equilibrium volume swelling ratio of the hydrogels V_r (volume of swollen gel/volume of the gel after preparation) was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass. V_r was calculated as $V_r = (D/D_0)^3$, where D and D_0 are the diameter of hydrogels after equilibrium swelling and after synthesis, respectively.

Mechanical Measurements

Uniaxial compression measurements were performed on gels after preparation. All the mechanical measurements were conducted in a thermostated room of 21 ± 0.1 °C. The stress-strain isotherms were measured by using an apparatus described before [21]. Briefly, cylindrical gel sample after preparation of 5.6 mm in diameter and 7.1 ± 0.7 mm in length was placed on a digital balance. A load was transmitted vertically to the gel through a road fitted with a PTFE end-plate. The force acting on the gel was calculated from the reading of the balance and the resulting deformation was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm. The force and the resulting deformation were recorded after 20 sec of relaxation. The measurements were conducted up to about 15 % compression. For uniaxial deformation, the statistical theories of rubber elasticity yield for Gaussian chains an equation of the form [22,23]:

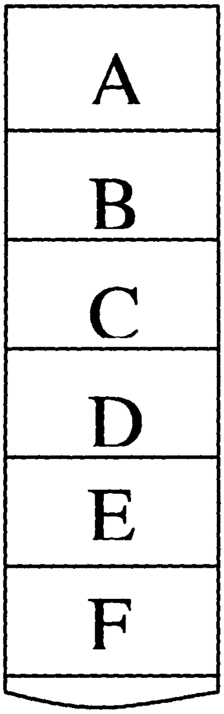
$$f = G\,(\alpha - \alpha^{-2}) \tag{1}$$

where f is the force acting on the unit cross-sectional area of undeformed gel sample, G is the elastic modulus of the sample, and α is the deformation ratio (deformed length/ initial length). As a general rule, the data fit to eq. (1), except at small compressions, where deviations due to surface effects appear. The treatment of the stress-strain data and calculation method of G were described in detail elsewhere [21]. The standard deviations in the values of G were less than 3 %.

Results and discussion

Position dependence of elastic modulus

In this section, the positional dependence of the elastic modulus of PAAm gels with 9 % BAAm content was investigated. PAAm gels in the forms of rods of 5.6 mm in diameter were prepared at an initial monomer concentration of 5.1 w/v %. After the gel preparation, five cylindrical gel samples, each about 7 mm in length, were cut from the same gel rod and their equilibrium swelling ratios V_r and elastic moduli G were measured. The location of the gel samples subjected to the measurements is illustrated in Figure 1. Visual observation showed separation of a liquid phase out of the gel phase during the free-radical crosslinking copolymerization. A in Figure 1 represents this liquid phase. As we reported before, separation of a liquid phase is due to the fact that the gel formed cannot absorb all the available reaction solution. As a result, a part of the solution separates out of the gel phase during the reactions. The liquid phase occupied a volume of about 20 % of the whole gelling system. Moreover, the gel sample that is the first neighbor to the liquid phase (B in Figure 1) always exhibited a lower modulus and a higher swelling ratio than all other gel samples. This is probably due to its contact with the solution phase, which slows down the reactions and reduces the crosslinking efficiency in this region. In order to eliminate the surface effect on the gel, we investigated the modulus variation along the gel regions C to F shown in Figure 1. Swelling measurements of the gel samples C to F showed that, within the limits of experimental error, the measured V_r values do not change along the gel rod. V_r values were found to be 1.3 ± 0.2.



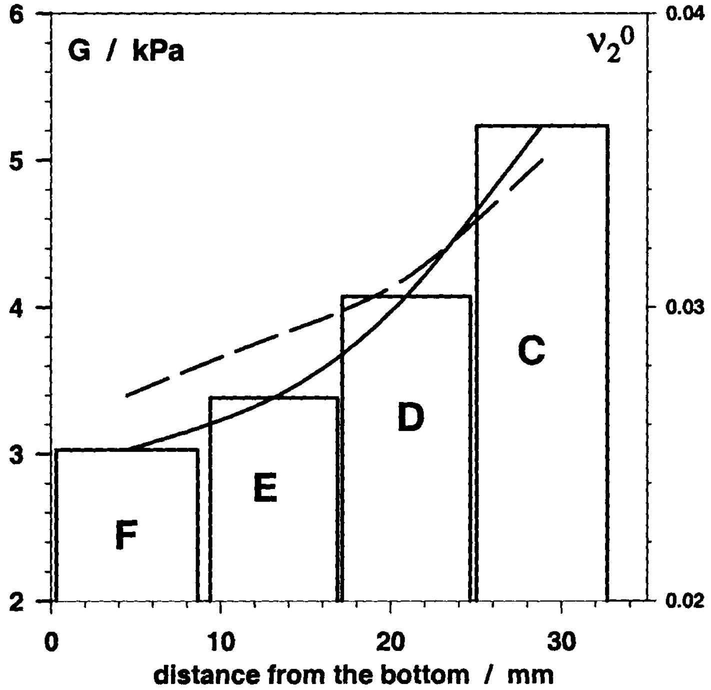


Fig. 1 (left): Location of PAAm gel samples subjected to swelling and mechanical measurements.

Fig. 2 (right): Variation of the elastic modulus G and the volume fraction of crosslinked polymer after the gel preparation v_2^0 along the PAAm gel rod with 9 % crosslinker content. The letters C to F represent the location of the samples given in Fig. 1. The bar width corresponds to the length of gel samples subjected to measurements. The solid curve shows modulus distribution. The dashed curve represents the variation of v_2^0 with the sample position.

The results of modulus measurements are shown in Figure 2 in the form of a bar graph. Here, the elastic modulus G is shown as a function of the location of the gel sample, in terms of the distance from the bottom of the gelling system. The bar width in the Figure corresponds to the length of the gel samples subjected to measurements. Solid curve represents the modulus variation along the gel. Figure 2 clearly shows that the elastic modulus G varies substantially as the location of measurement is "scanned" within the gel. G increases continuously with increasing distance from the bottom of the gel rod, indicating that the effective crosslink density of the network chains increases along the same direction within the gel. It is important to observe that the variation of modulus is reproducible when measurements are repeated along the same path with different gel rods. Thus, although the equilibrium swelling ratio with respect to after preparation state remains constant along the gel, the elastic modulus of PAAm gels with 9 % BAAm strongly depends on the location at which the mechanical measurements are carried out.

Position dependent elastic moduli in PAAm gels should have the consequence that the gel rod after preparation will absorb the polymerization solvent (water) heterogeneously. That is, the lower part of the gel is expected to be in a more diluted state than the upper part. In order to check this point, we used Flory's theory of swelling equilibrium for affine networks [22]:

$$\ln(1-v_2)+v_2+\chi v_2^{2}+\frac{\rho}{\overline{M}_c}V_1\left(v_2^{1/3}\,v_2^{0\,2/3}-v_2/2\right)=0 \tag{2}$$

where v_2 is the volume fraction of polymer network in the equilibrium swollen gel, χ is the polymer - solvent interaction parameter, ρ is the polymer density, V_1 is the molar volume of solvent, $\overline{M}_c$ is the molecular weight of the network chains, and v_2^0 is the volume fraction of polymer network after the gel preparation. Moreover, the elastic modulus of an affine network after its preparation G relates to the crosslink density through the relation [22]:

$$G=\frac{\rho}{\overline{M}_c}RTv_2^0 \tag{3}$$

where R is the gas constant and T is the temperature. Since $v_2=v_2^0/V_r$, Combining eqs. (2) and (3) leads to:

$$\ln\left(1-v_2^0/V_r\right)+v_2^0/V_r+\chi\left(v_2^0/V_r\right)^2+\frac{G}{RT}V_1\left(V_r^{-1/3}-\frac{1}{2}V_r^{-1}\right)=0 \tag{4}$$

Using the values χ = 0.48 [16], V_1 = 18 mL/mol, V_r = 1.3, R = 8.314 J/mol-K, and T = 294 K, together with the experimentally determined G values, eq. (4) was solved for v_2^0, which is a measure of the degree of dilution of the gel after preparation. The calculation results are shown in Figure 2 as the dashed curve plotted as a function of the distance from the bottom of the gelling system. It is seen that ν_2^0 decreases continuously from gel C to F, indicating that the lower section of the gel after preparation is in a more diluted state than its upper section. This also means that the equilibrium swelling ratio with respect to dry state, i.e., $1/\nu_2$ is higher in the lower section than that in the upper section.

Crosslinker effect

As a next step, the extent of the modulus variation along the gel rod was investigated as a function of the crosslinker (BAAm) content. For this purpose, a series of gel rods with various BAAm contents between 2.6 and 20.6 % were prepared. From each gel rod, two gel samples were taken; one from the upper section (Section C in Figure 1) and the other from the lower section (Section F in Figure 1), each 7.1 ± 0.7 mm in length. These samples were subjected to swelling and mechanical measurements. As expected, the swelling ratio decreased from 2.6 to 1.2 with increasing crosslinker content from 2.6 to 20.6 %. However, swelling measurements carried out on samples taken from the upper and lower sections of the same gel showed that the measured V_r values do not change along the gel rod.

Both the gel appearance and the elastic modulus were found to depend strongly on the location of the measurements as well as on the overall crosslinker concentration. The visual appearance of PAAm gels prepared at various crosslinker (BAAm) contents is schematically illustrated in Figure 3. Here, the appearances of the upper and lower sections of the gel samples are shown separately for each crosslinker content. In Figure 4, the elastic moduli of the gels G are shown as a function of the crosslinker concentration. The filled and open symbols represent G values measured in the upper and lower sections, respectively. One has to distinguish three regimes depending on the crosslinker concentration:

1. **2.6 % BAAm:** This is the usual BAAm concentration for the hydrogel synthesis reported in many literatures. The gels are transparent and their elastic moduli G do not depend on the location at which the mechanical measurements are carried out. The value G = 2.7 kPa indicates existence of a large number of cycles or multiple crosslinks in the PAAm network [2,5].
2. **Between 2.6 and 9 % BAAm:** The lower sections become increasingly opaque but the upper sections remain semi-transparent (Figure 3). The elastic modulus G of the upper section is higher than that measured in the lower section and the distance between these two G values increases with increasing crosslinker concentration from 2.6 to 9 % BAAm. (Figure 4). Moreover, G of the upper section rapidly increases with increasing crosslinker concentration, while that of the lower section increases only slightly.
3. **Above 9 % BAAm:** G rapidly decreases above 9 % BAAm and the values measured in both sections approach each other at higher BAAm concentrations. In this regime, both sections are opaque and the degree of opacity increases with increasing BAAm concentration.

BAAm contents (from left to right) = 2.6, 5.1, 7.7, 9, and ≥ 12.9 wt %. T = transparent, ST = semi-transparent, O = opaque

From these findings, we propose the following mechanism for the development of the

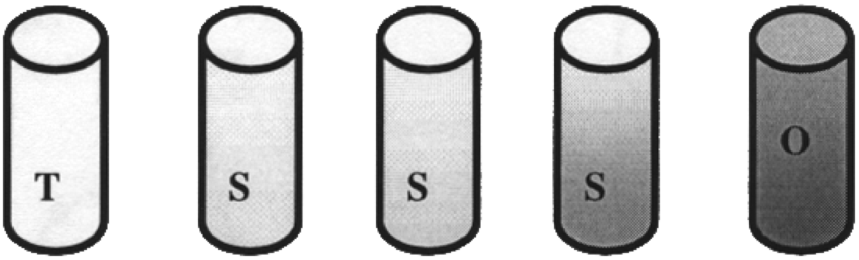
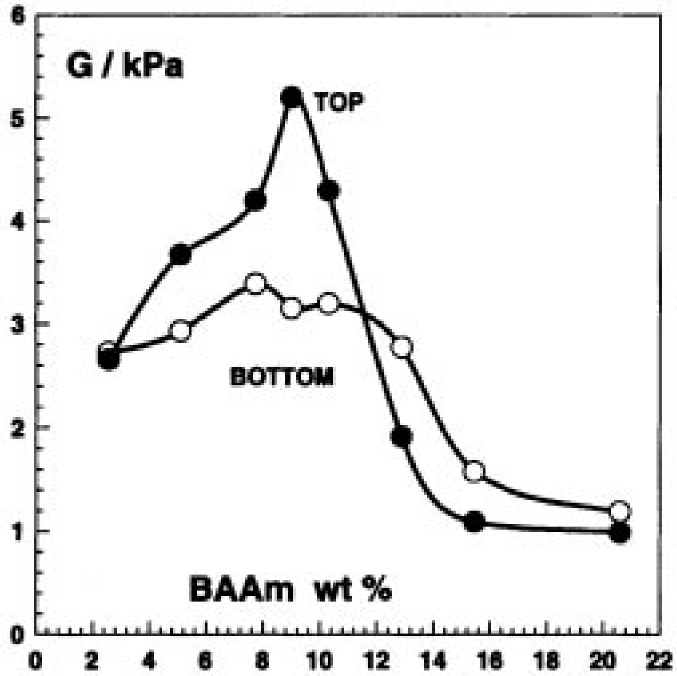


Fig. 3: Visual appearance of PAAm gels. Initial monomer concentration = 5.1 w/v%.

network inhomogeneities in PAAm gels: When the polymerization is initiated by the decomposition of KPS molecules, the primary radicals formed start to grow by adding the monomer AAm and the crosslinker BAAm. Initially, the primary molecules contain AAm units, BAAm units with one vinyl group unreacted (i.e., with pendant vinyl groups) and BAAm units involved in cycles. As the time goes on, more and more primary molecules are formed so that the intermolecular crosslinking reactions between the primary molecules may also occur during the polymerization. Previous works show, however, that at least 80% of the pendant vinyl groups in this gelling system are consumed by cyclization reactions [2,3,5,7]. Thus, cyclization clearly dominates over the intermolecular crosslinking reactions in AAm-BAAm copolymerization. Since every cycle reduces the coil dimension of the molecules as well as the solvent content inside the coil, the structure of the polymers formed is rather compact and can be considered as clusters. The higher the crosslinker content, the higher is the cyclization density of the clusters, or the lower is their solvent content. When a cluster reaches to a density, which overcomes the density of the solution it falls down to the reaction system. This point corresponds to 7.7 % BAAm concentration, at which the lower section of the gel becomes opaque while the upper section remains transparent (Figure 3). The semi-transparency of the upper section of the gel as the crosslinker content increases from 5.1 to 9 % is a consequence of the sedimentation of the polymer clusters crossing the critical density (Figure 3).

It is to be noted that previous works also indicate sedimentation of intramolecularly crosslinked polymer particles (microgels) during the gel formation process in dilute solutions [7,10]. Using gravimetric, dilatometric and in-situ photon transmission techniques, we recently studied the gel formation and growth process in AAm - BAAm copolymerization [12,24]. The experimental conditions were identical to those of the present work. The results show sedimentation of microgel-like particles during the reactions. The gel point, which is usually a point at which the system changes from liquid to solid-like state, is for the present system a point at which gel particles in the lower part of the reactor start to appear [12]. These observed deviations from the classical picture of gel formation are due to the high extent of cyclization reactions [2,3] as well as due to the high degree of dilution of the gelling system [12].



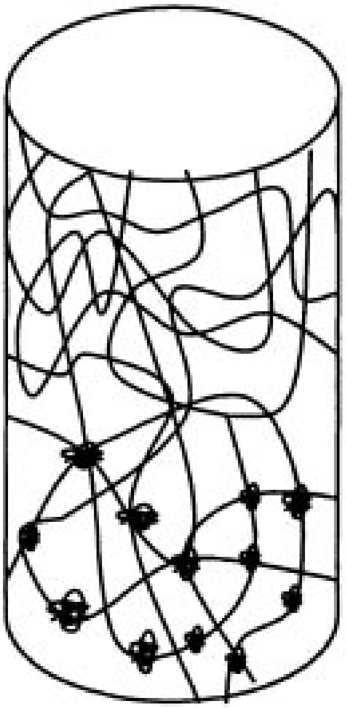


Fig. 4 (left): Elastic moduli of the gels after preparation G shown as a function of the crosslinker (BAAm) concentration. The filled and open symbols represent the values measured in the upper and lower sections, respectively. Initial monomer concentration = 5.1 w/v%.

Fig. 5 (right): Schematic representation of PAAm gels formed by free-radical mechanism.

Comparing the reactivities of the monomers AAm and BAAm in free-radical copolymerization, BAAm reactivity is at least twice the AAm reactivity due to the existence of two vinyl groups on each BAAm molecule. Therefore, the molecules formed earlier should contain more BAAm units than those formed later. Due to the rapid consumption of BAAm monomer during polymerization, the density of the clusters will decrease as the monomer conversion increases and, at high conversion degrees, their structure will approach to that of the primary molecules. Thus, the later formed molecules having a lower density than those formed earlier remain in the solution phase and build the upper sections of the gel samples. Increasing crosslinker content increases both the size and the number of clusters in the system. As a result, the interconnected clusters in the lower section of the reaction system grow and finally reach to the upper section. This point corresponds to 12.9 % crosslinker content, at which both sections of the gel become opaque (Figure 3). When this point is crossed, both sections behave identical.

From this picture, one can identify two different network structures in the same gel system, as schematically illustrated in Figure 5; one of interconnected clusters and the other of primary molecules. The network structure changes gradually from one to another along the gel sample. At 2.6 % BAAm (or below) and above 9 % BAAm, we have only one of the two network structures in the gel system. Between 2.6 and 9 % BAAm, the relative volumes of the network structures vary depending on the crosslinker concentration.

The results of the elastic moduli measurements shown in Figure 4 can also be explained using this picture. Each cluster consists of many polymer chains attracted and crosslinked each other. The agglomeration of these clusters to form an infinite network may occur through their peripheral pendant vinyls and radical ends, while those in their interior remain intact. This means that a large number of BAAm units are wasted inside the clusters and each cluster acts as a single junction point. On the other hand, as the density of the clusters decreases, the pendant vinyl groups become more accessible for the macroradicals of other molecules and this facilitates the intermolecular crosslinking reactions. Thus, the crosslinking efficiency in the network of clusters is necessarily lower than that of a network of primary molecules. This leads to the observed lower moduli of the lower sections of the gel compared to the upper sections. Increasing crosslinker content only increase the compactness of the clusters without changing much the distance between them so that the moduli do not change much in the lower sections of the gels. The existence of only one network structure at 2.6 % BAAm or above 9 % BAAm contents is reflected in the mechanical measurements with the approach of the moduli of both sections towards each other. Moreover, the rapid decrease of the moduli above 9 % BAAm indicates formation of heterogeneous PAAm networks. Heterogeneous structures are known to form as a result of a phase separation in the network formation system [10, 14]. After passing a critical crosslinker content, the infinite network cannot absorb all the reaction solution present in the polymerization and separates into two phases; gel and solution (water) phases. Further crosslinking reactions fix the two-phase structure in the final gel. Heterogeneous gels are known to exhibit lower moduli than the corresponding homogeneous or inhomogeneous gels [25]. Elastic modulus data indicate that the heterogeneity in PAAm gels starts to appear above 9 % BAAm content. Calculation of the degree of dilution of the network after preparation using eq. (4) together with the experimental modulus and swelling data showed that, as in the previous section, the lower section of each gel sample is in a more diluted state than the upper section between 2.6 and 9 % BAAm content.

We also tested PAAm inhomogeneities using gel samples prepared at various ionic comonomer contents between 0 and 30 mol % but at a fixed crosslinker content (2.6 wt %). 2-Acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS) was used as the ionic comonomer of AAm. The results of the elastic modulus measurements at various locations of the gel samples showed that the moduli do not change along the gel. This means that, in contrast to the crosslinker BAAm, the existence of ionic groups in the gel does not affect the inhomogeneity. All these ionic gel samples prepared were transparent.

In conclusion, we introduced a new technique to study the inhomogeneities in PAAm gels. It was shown that the elastic modulus of gels varies depending on the location of the mechanical measurements. The extent of modulus variation increases with increasing crosslinker content from 2.6 to 9 %. A mechanism was proposed for the development of gel inhomogeneities in PAAm gels. It is to be noted that more experimental data on hydrogels of different compositions are needed for the generalization of the proposed picture for the gel inhomogeneities.

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