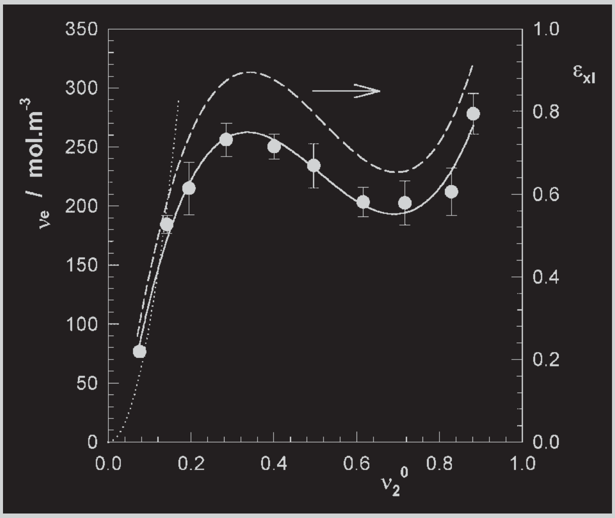
**Summary:** The equilibrium swelling degree, modulus of elasticity and the spatial inhomogeneity of poly(*N*,*N*-dimethylacrylamide) (PDMAAm) hydrogels were investigated over the entire range of the initial monomer concentration. The degree of dilution of the networks after their preparation was denoted by $v_2^0$, the volume fraction of crosslinked polymer after the gel preparation. The linear swelling ratio of the gels increased linearly with increasing $v_2^0$. Depending on the value of $v_2^0$, three different gel regimes were observed: (1) For $v_2^0 < 0.3$, increasing $v_2^0$ decreases the extent of cyclization during crosslinking so that the effective crosslink density of gels increases with rising $v_2^0$. (2) For $0.3 < v_2^0 < 0.7$, increasing $v_2^0$ reduces the accessibility of the pendant vinyl groups during crosslinking due to steric hindrance at high polymer concentrations. As a result, the effective crosslink density of gels decreases with increasing $v_2^0$. (3) For $v_2^0 > 0.7$, the modulus of elasticity increases sharply with increasing $v_2^0$ due to the increasing extent of chain entanglements in this high concentration regime. Static light scattering measurements on the gels show that the degree of spatial gel inhomogeneity in PDMAAm gels attains a maximum value at $v_2^0 = 0.06$. The appearance of a maximum as well as the $v_2^0$-dependence of scattered light intensities from gels was successfully reproduced by the theory proposed by Panyukov and Rabin.



Effective crosslink density $\nu_e$ of the hydrogels shown as a function of $v_2^0$.

# Swelling, Elasticity and Spatial Inhomogeneity of Poly(*N*,*N*-dimethylacrylamide) Hydrogels Formed at Various Polymer Concentrations

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**Keywords:** elasticity; gels; inhomogeneity; light scattering; poly(*N*,*N*-dimethylacrylamide)

## Introduction

Polyacrylamide (PAAm) gels have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. These materials are obtained by the free-radical crosslinking copolymerization of acrylamide (AAm) and *N*,*N*′-methylenebis(acrylamide) (BAAm) monomers. Since the monomers are solid at the usual polymerization temperature, it is necessary to carry out the polymerization reactions in an aqueous solution of the monomers. Several studies have shown that the hydrogel structure and therefore the hydrogel properties strongly depend on the initial monomer concentration.[1–10] Increasing the amount of water causes the polymer chains to disentangle so that the network formed in a dilute solution can swell highly when exposed to a good solvent. On the other hand, decreasing the polymer concentration increases the probability of cyclization and multiple crosslinking reactions during crosslinking, so that a large fraction of the crosslinker BAAm is wasted through ineffective crosslinks.[11,12] As a result, the network structure formed becomes increasingly loose as the degree of dilution increases.

No continuous networks are formed above a critical amount of solvent.[11] Shibayama et al. reported that the linear swelling ratio of swollen poly(*N*-isopropylacrylamide) (PNIPA) hydrogels was independent of the initial monomer concentration.[13] They derived scaling rules showing the relationship between the polymer volume fraction in the equilibrium swollen gel and the monomer concentration. Bromberg et al. proposed a simple statistical model to estimate the crosslink density of gels from the gel synthesis parameters.[14] Using this model, they were able to explain the swelling behavior of both non-ionic and ionic hydrogels from their synthesis conditions. Although several studies have been reported on the properties of hydrogels, there is still no quantitative correlation between the synthesis parameters of hydrogels and their physical properties in existence.

It has also been shown experimentally and theoretically that PAAm hydrogels exhibit inhomogeneous crosslink density distributions, known as spatial gel inhomogeneity.[15,16] Since the gel inhomogeneity is closely connected to the spatial concentration fluctuations, scattering methods such as light scattering, small-angle X-ray scattering and small-angle neutron scattering have been employed to investigate the spatial inhomogeneities.[17–31] The gel inhomogeneity can be manifested by comparing the scattering intensities from the gel and from a semi-dilute solution of the same polymer at the same concentration. The scattering intensity from gels is always larger than that from the polymer solution. The excess scattering over the scattering from the polymer solution is related to the degree of inhomogeneity in the gels. In general, the gel inhomogeneity increases significantly with the crosslink density, but decreases with the ionization degree of the hydrogels. Recently, we have shown that the initial monomer concentration also significantly affects the degree of inhomogeneity in PAAm gels.[32] An inflection point was observed in the excess scattering versus monomer concentration plot, at which the inhomogeneity attained a maximum value. Contrary to the experimental findings, classical theories predict that the scattered intensity from gels should decrease when increasing the crosslinker or the total monomer concentration.[15,16] Moreover, several functional forms for the excess scattering from gels have been proposed empirically to interpret scattering results from gels.[33–38] However, these functions assume the functional dependence of the excess scattering on the scattering vector without detailed discussion of its validity. Recently, a statistical theory was proposed to describe the structural factor of gels depending on the thermodynamic conditions after the gel preparation as well as at the state of the measurements.[39]

In the present work, we have prepared a series of gels based on *N*,*N*-dimethylacrylamide (DMAAm) monomer at various polymer network concentrations but at a fixed chemical crosslink density. The selection of DMAAm as a monomer is due to the fact that it is a liquid at room temperature and is fully miscible with water. Thus, poly(*N*,*N*-dimethylacrylamide) (PDMAAm) hydrogels could be prepared in aqueous solutions at monomer concentrations from a few percent up to 100% (without the use of a solvent). In this way, we were able to investigate the hydrogel properties over the whole range of polymer concentrations, which have not been reported previously. The gels were characterized by swelling and elasticity tests as well as by light scattering measurements at a state just after their preparation. An equivalent semi-dilute PDMAAm solution served as a reference in the understanding of the inhomogeneities in gels. As will be seen below, several interesting features of PDMAAm gels were observed, which have been explained using the available theories.

## Experimental Part

### *Materials*

*N*,*N*-dimethylacrylamide (DMAAm, Fluka), *N*,*N*′-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were used as received. APS and TEMED stock solutions were prepared by dissolving 0.080 g of APS and 0.250 ml of TEMED separately in 10 ml of water.

### *Synthesis of Hydrogels*

PDMAAm gels were prepared by the free-radical crosslinking copolymerization of DMAAm and BAAm in aqueous solution at 5 °C in the presence of $3.51 \times 10^{-3}$ M of APS initiator and 0.25 vol.-% TEMED accelerator. The initial molar concentration of the monomers, denoted by $C_0$, was varied between 0.37 and 9.7 M. The crosslinker ratio $X$ (mole ratio of the crosslinker BAAm to the monomer DMAAm) was fixed at 1:83. To illustrate the synthetic procedure, we give details for the preparation of a gel at $C_0 = 1.45$ M. APS stock solution (1.0 ml), DMAAm (1.47 ml), BAAm (0.0264 g) and water (6.50 ml) were mixed in a 10 ml graduated flask. After bubbling nitrogen for 15 min, TEMED stock solution (1.0 ml) was added to the mixture. The solution was then poured into several glass tubes with internal diameters of 4.5–5 mm which were about 100 mm in length. The glass tubes were sealed, immersed in a thermostated water bath at 5 °C and the polymerization was conducted for 1 d. For the preparation of hydrogels at $C_0 > 8.8$ M, the reactions were carried out one day at 5 °C and another day at 70 °C.

### *PDMAAm Network Concentration at the Stage of Gel Preparation*

The degree of dilution of the networks after their preparation was denoted by $v_2^0$, the volume fraction of crosslinked polymer after the gel preparation. In order to determine $v_2^0$, PDMAAm hydrogels after preparation were first swollen in water to extract non-polymerizable or soluble components and then

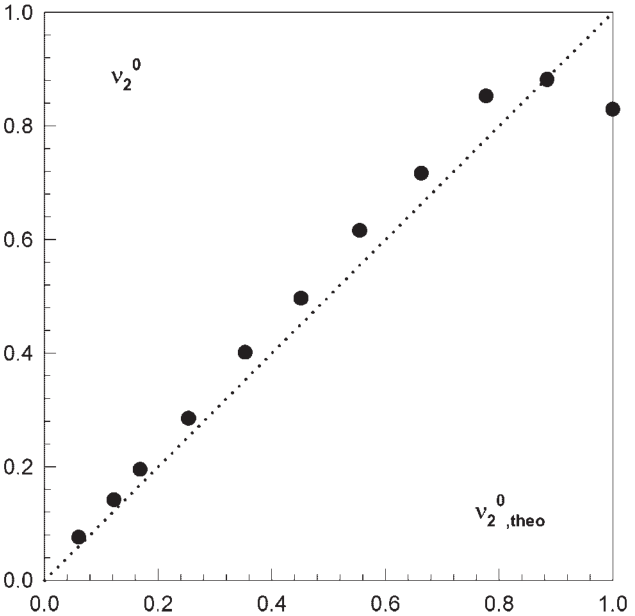

Figure 1. Experimentally determined $\nu_2^0$ of the hydrogels shown as a function of its theoretical value ($\nu_{2,\text{theo}}^0$).$\nu_{2,\text{theo}}^0$ was calculated from the initial monomer concentration used in the gel preparation and assuming that the monomer conversions were complete after the crosslinking copolymerization. The dotted line shows the relation $\nu_2^0 = \nu_{2,\text{theo}}^0$.

dried to constant mass. $\nu_2^0$ was calculated as

$$\nu_2^0 = \left[1 + \frac{(q_F - 1)\rho}{d_1}\right]^{-1} \tag{1}$$

where $q_F$ is the dilution degree after the gel preparation (mass of gel after preparation : mass of dried gel), $\rho$ is the polymer density (1.21 $g \cdot ml^{-1}$) and $d_1$ is the solvent density (1.00 $g \cdot ml^{-1}$). Moreover, assuming that the monomer conversions were complete after the crosslinking copolymerization, the theoretical value of $\nu_2^0$ can also be calculated from the initial molar concentration of the monomers $C_0$ as $\nu_{2,\text{theo}}^0 = 10^{-3}\, C_0 V_r$, where $V_r$ is the molar volume of the PDMAAm repeat units (81.6 $ml \cdot mol^{-1}$).

Figure 1 shows the experimentally determined $\nu_2^0$ of PDMAAm hydrogels plotted as a function of its theoretical value $\nu_{2,\text{theo}}^0$. The straight line representing the relation $\nu_2^0 = \nu_{2,\text{theo}}^0$ gives a good fit with the data, indicating that, under the reaction conditions, the monomer conversions and the gel fractions are complete, as long as $\nu_{2,\text{theo}}^0 < 1$.

### *Swelling Measurements in Water*

The hydrogels in the form of rods of 4 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at 24 ± 0.5 °C. In order to reach swelling equilibrium, the hydrogels were immersed in water for at least two weeks, replacing the water every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples. To achieve good precision, three measurements were carried out on samples of different lengths taken from the same gel. The linear swelling ratio $D/D_0$ was determined by measuring the diameter of the hydrogel samples after equilibrium swelling in water, $D$, and after synthesis, $D_0$, with a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). Figure 2 shows a plot of $D/D_0$ vs. $\nu_2^0$ of the PDMAAm hydrogels and indicates that $D/D_0$ increases linearly with increasing $\nu_2^0$ from 0.08 to 1. The normalized volume of the equilibrium swollen hydrogels $V_{eq}$ (volume of equilibrium swollen gel/volume of the gel just after preparation) and the volume fraction of crosslinked polymer in the equilibrium swollen gel $\nu_{2,eq}$ were calculated as:

$$V_{eq} = (D/D_0)^3 \tag{2}$$

$$\nu_{2.eq} = \nu_2^0 / V_{eq} \tag{3}$$

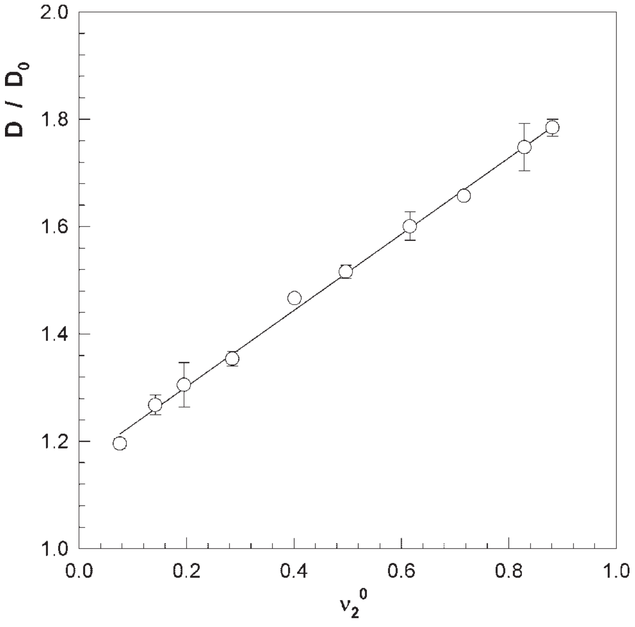

Figure 2. Linear swelling ratio $D/D_0$ of the hydrogels shown as a function of $\nu_2^0$.

### *Mechanical Measurements*

Uniaxial compression measurements were performed on the gels just after their preparation as well as after equilibrium swelling in water. All the mechanical measurements were conducted in a thermostated room at 24 ± 0.5 °C. The stress-strain isotherms were measured by using an apparatus described elsewhere.[40] The elastic modulus $G$ was determined from the slope of linear dependence:

$$f = G(\alpha - \alpha^{-2}) \tag{4}$$

where $f$ is the force acting per unit cross-sectional area of the undeformed gel specimen and $\alpha$ is the deformation ratio (deformed length/initial length). Typical stress-strain data, correlated according to Equation (4), are shown in Figure 3 for PDMAAm hydrogels with varying polymer network concentrations $\nu_2^0$.

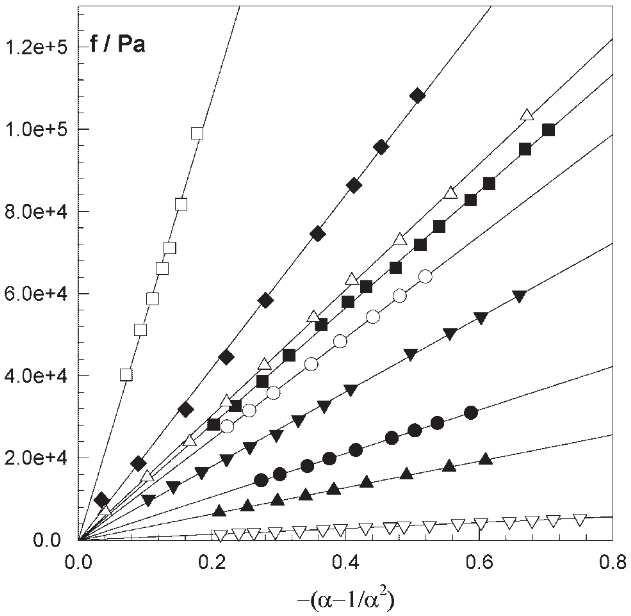

Figure 3. Typical stress-strain data for PDMAAm hydrogels just after their preparation. The crosslinked polymer concentrations $v_2^0$: 0.076 (▽), 0.142 (▲), 0.195 (●), 0.286 (▼), 0.401 (○), 0.496 (■), 0.616 (△), 0.717 (◆), 0.778 (□).

For a network of Gaussian chains, the elastic modulus $G$ of gels swollen to equilibrium is related to the effective crosslink density $v_e$ by:[41,42]

$$G = A v_e RT \left(v_2^0\right)^{2/3} \left(v_{2,\mathrm{eq}}\right)^{1/3} \tag{5}$$

where the front factor A equals 1 for an affine network and 1−2/$\phi$ for a phantom network, where $\phi$ is the functionality of the crosslinks and $R$ and $T$ take their usual meanings. Since $v_2 = v_2^0$ for the hydrogels just after preparation, the elastic modulus $G_0$ after preparation becomes

$$G_0 = A v_e RT v_2^0 \tag{6}$$

From Equation (3), (5) and (6), the reduced modulus $G_r$, defined as the ratio of the elastic modulus of the equilibrium-swollen gel to that of the same gel after its preparation, is given for a network of Gaussian chains by:

$$G_r = \frac{G}{G_0} = \left(\frac{v_{2,\mathrm{eq}}}{v_2^0}\right)^{1/3} = V_{\mathrm{eq}}^{-1/3} \tag{7}$$

### *Light Scattering Experiments*

For the light scattering measurements, the crosslinking polymerizations were carried out in light scattering cuvettes. All glassware was kept dust-free by rinsing in hot acetone prior to use. The solutions were filtered through Nylon filters (pore size = 0.2 μm) directly into the cuvettes. This process was carried out in a dust-free glovebox. All the gels subjected to light scattering measurements were clear and appeared homogeneous to the eye. For calculation of the excess scattering from the gels, all the crosslinking polymerizations were repeated under the same experimental conditions, omitting the crosslinker BAAm.

The light scattering measurements were carried out at 24 °C in a modernized Sofica apparatus, equipped with a He-Ne laser ($\lambda = 632.8$ nm) and a computerized data acquisition system. The scattered light intensities were recorded from 50° to 150° which corresponds to the scattering vector $q$ range $1 \times 10^{-3} - 2.2 \times 10^{-3}$ Å$^{-1}$, where $q = (4\pi n/\lambda)\sin(\theta/2)$, $\theta$ is the scattering angle, $\lambda$ is the wavelength of the incident light in vacuum and $n$ is the refractive index of the medium. The light scattering system was calibrated against a toluene standard. To obtain the ensemble averaged light scattering intensity of gels, three cycles of measurements with a 60° rotation of the vial between each cycle were averaged.

## Results and Discussion

In the first subsection, we discuss the monomer concentration dependences of the equilibrium swelling behavior and the elasticity of PDMAAm hydrogels. In the second subsection, we discuss the spatial inhomogeneity in gels and interpret the experimental observations.

### *Elasticity of Gels*

PDMAAm hydrogels with a fixed crosslinker ratio $X = 1/83$ were prepared at various concentrations $v_2^0$ ranging from dilute to concentrated solutions. In Figure 4, the volume fraction of crosslinked polymer in the equilibrium swollen gel $v_{2,\mathrm{eq}}$ and the elastic moduli of gels after preparation $G_0$ and after equilibrium swelling in water $G$ are shown as symbols plotted as a function of $v_2^0$. Using the $G_0$ and $v_2^0$ of the hydrogels together with Equation (6) one may calculate the effective crosslink densities $v_e$ of the hydrogels. The results for a phantom network model ($\phi = 4$) are shown in Figure 5 as symbols plotted against $v_2^0$. The solid curves in Figure 4 and 5 only show the trend of the data. The dashed curve in Figure 5 represents the crosslinking efficiency $\varepsilon_{\mathrm{xl}}$, calculated using the equation

$$\varepsilon_{\mathrm{xl}} = v_e / v_{\mathrm{chem}} \tag{8}$$

where $v_{\mathrm{chem}}$ is the chemical crosslink density of the hydrogels, which would result if all the crosslinker (BAAm) molecules formed effective crosslinks in the hydrogel (Since $X = 1{:}83$, $v_{\mathrm{chem}} = 294$ mol · m$^{-3}$ and constant over all $v_2^0$ range). Thus, $\varepsilon_{\mathrm{xl}}$ gives the fraction of the crosslinker BAAm molecules consumed in the formation of effective crosslinks. Depending on the value of $v_2^0$, three different regimes can be distinguished from Figure 4 and 5:

1) For $v_2^0 < 0.3$, both $v_{2,\mathrm{eq}}$ and $v_e$ are increasing functions of $v_2^0$. Thus, increasing the polymer network concentration at the gel preparation ($v_2^0$) results in decreased swelling ratios and increased effective crosslink densities of the hydrogels. This is expected due to the fact that increasing polymer concentration during the gel formation

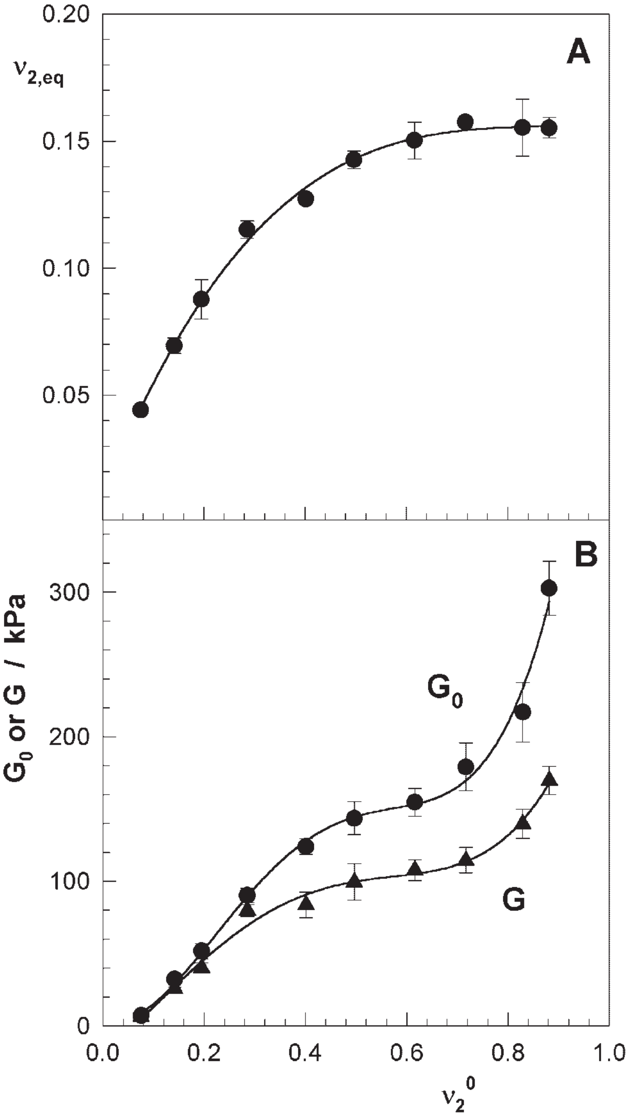

Figure 4. (A) The volume fraction of crosslinked polymer in the equilibrium swollen gel $v_{2,\mathrm{eq}}$ shown as a function of $v_2^0$. (B) Elastic moduli of gels after preparation $G_0$ and after equilibrium swelling in water $G$ shown as a function of $v_2^0$.

decreases the probability of cyclization and multiple crosslinking reactions. Indeed, the crosslinking efficiency $\varepsilon_{\mathrm{xl}}$, shown in Figure 5 by the dashed curve, rapidly increases from 0.2 to 0.9 on rising $v_2^0$. The importance of cyclization at low $v_2^0$ can also be seen from the $v_e$ vs. $v_2^0$ dependence, which intersects the abscissa at a non-zero $v_2^0$ value.

2) For $0.3 < v_2^0 < 0.7$, $v_{2,\mathrm{eq}}$ increases further, but only slightly, while both the effective crosslink density and the crosslinking efficiency decrease with increasing $v_2^0$. In this regime, since the polymer concentration is relatively high (30–70% after complete monomer conversion), the pendant vinyl groups during the gel formation tend to have lower relative reactivities because of the steric hindrance. Previous works indeed show that the accessibility of the pendant vinyl groups for other polymer molecules is strongly reduced at high monomer concentrations.[7,11,43–45] Calculations indicate a 1–2 orders of magnitude decrease in the average reactivity of pendant vinyls for intermolecular reactions compared to the monomeric vinyls. As a result, a fraction of the pendant vinyl groups remains unreacted in the final hydrogel leading to the observed decrease in the crosslink density of gels on rising $v_2^0$. The results thus show that the gel passes from the first to the second regime at $v_2^0 = 0.3$, at which the gel crosslink density becomes maximum. Going downward from the maximum point to the lower or higher polymer concentrations, the crosslinking efficiency $\varepsilon_{\mathrm{xl}}$ decreases (Figure 5), due to the cyclization and steric effects, in the first and second regimes, respectively.

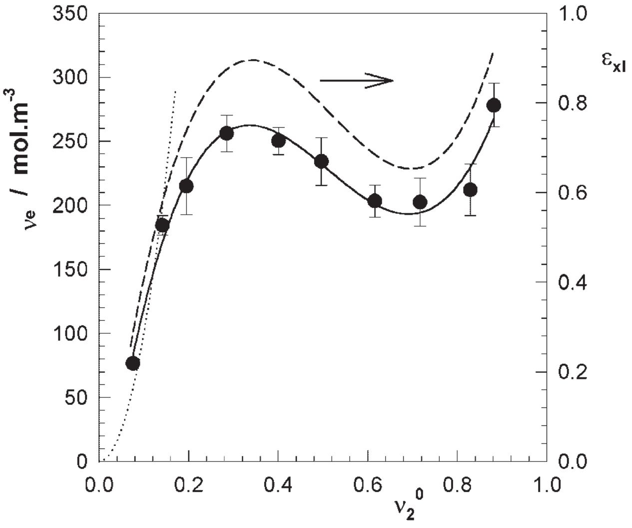

Figure 5. Effective crosslink density $v_e$ of the hydrogels shown as a function of $v_2^0$. $v_e$ was calculated from the elastic moduli of the hydrogels at the state of preparation. For calculations, we assumed phantom network behavior. The solid curve shows the trend of the data. The crosslinking efficiency $\varepsilon_{\mathrm{xl}}$ is also shown in the Figure by the dashed curve. The dotted curve was calculated using Equation (12).

3) For $v_2^0 > 0.7$, $v_{2,\mathrm{eq}}$ does not change with $v_2^0$ but the effective crosslink density $v_e$ increases sharply with increasing $v_2^0$. The rapid increase of $v_e$ with increasing monomer concentration may be interpreted as a result of the increasing extent of chain entanglements in this high concentration regime.

Now we should mention the other studies about the variation of the swelling degree and the elasticity of gels depending on the monomer concentration. Baker et al. studied a series of cationic PAAm gels formed at $X = 1{:}500$ but at varying $v_2^0$ between 0.11 and 0.30.[5] They reported that the degree of swelling decreases while the elastic modulus increases with increasing $v_2^0$. The negative deviation in the effective crosslink density of gels from the phantom theory was explained with cyclization, while the positive deviation at high $v_2^0$ was attributed to the chain entanglements. Shibayama et al. observed that the linear swelling ratio $D/D_0$ of PNIPA hydrogels prepared at $X = 1{:}80$ is independent of the initial monomer concentration in the range $v_2^0 = 0.03-0.08$.[13] The invariance of $D/D_0$ with $v_2^0$ was explained with chain entanglements acting as additional crosslink points, whose number increases with increasing concentration. Our experimental data with PDMAAm gels show, however, a linear increase of $D/D_0$ with concentration (Figure 2).

In the statistical model proposed by Bromberg et al., the gelation process is treated as a set of random walks starting from the initiator and proceeding by picking up the monomers and the crosslinker.[14] Since in a random walk the path length (the end-to-end distance) of a chain after $g$ steps is $g^{1/2}$, the polymer segment concentration $C$ during the crosslinking copolymerization scales with $g/g^{3/2} = g^{-1/2}$, or:[14]

$$g \approx C^{-2} \tag{9}$$

After $g$ steps, the growing chain will hit another chain. The model assumes that the probability $p$ that the growing chain will meet a crosslinker unit on another chain is equal to the number fraction of the crosslinker molecules in the reaction system, i.e.,

$$p = X/(1+X) \cong X \quad (\text{for } X \ll 1) \tag{10}$$

where $X$ is the crosslinker ratio. Thus, after $1/p$ hits, the growing chain will succeed to form an effective crosslink. The network chain length $N$ will then be equal to:

$$N = \frac{g}{p} = C^{-2}X^{-1} \tag{11}$$

Since $N \approx v_e^{-1}$, $C \approx v_2^0$, $X$ is fixed in our experiments and from Equation (11), one obtains

$$v_e \approx (v_2^0)^2 \tag{12}$$

indicating that the effective crosslink density of PDMAAm gels should scale with the second power of the monomer concentration $v_2^0$. The dotted curve in Figure 5 represents $v_e$ versus $v_2^0$ dependence predicted by Equation (12). It is seen that the model only predicts the initial increase in the crosslink density with concentration $v_2^0$. Over the whole range of $v_2^0$, the real behavior of gels strongly deviates from the prediction of Equation (12). This is mainly due to Equation (10), which assumes a constant probability $p$ for the growing chain to form crosslinks. In real systems, $p$ varies depending on the microenvironment of the growing chains because of the intramolecular crosslinking reactions as well as conversion dependent reactivities of the pendant vinyl groups, which were not considered in the model.

Furukawa presented an equation predicting the equilibrium swelling of gels depending on the monomer concentration.[8] This formula is interesting and takes into account the effect of entanglements. However, there are six adjustable parameters in Furukawa's equation so it does not allow a definitive conclusion regarding the suitability of the model. Kinetic theories connecting the initial conditions of the gel forming systems to the final gel properties also require a large number of kinetic parameters.[46] Our experimental results show three different regimes for the dependence of the gel properties on the monomer concentration, which have not been predicted by the theories.

In Figure 6A, the reduced modulus $G_r$ of the hydrogels is plotted against the equilibrium gel volume $V_{eq}$. The solid curve is the best fit to the experimental data, which gives an exponent $-0.32 \pm 0.05$, close to the theoretical value of $-1/3$ (Equation (7)). Thus, PDMAAm gels swollen to equilibrium in water behave as Gaussian. Since the network chains are Gaussian in their equilibrium swollen states, the Flory-Rehner equation can be used to calculate the polymer-solvent interaction parameter $\chi$ of the system.[41] $\chi$ was calculated from the expression for phantom chains as:

$$\chi = -\frac{\ln(1 - v_{2,eq}) + v_{2,eq} + 0.5 v_e V_1 (v_{2,eq})^{1/3} (v_2^0)^{2/3}}{(v_{2,eq})^2} \tag{13}$$

The calculation results of $\chi$ are shown in Figure 6B plotted against the equilibrium polymer volume fraction $v_{2,eq}$. The straight line through the experimental points in the range of $v_{2,eq} = 0.04-0.16$ is obtained by least squares as:

$$\chi = \chi_1 + \chi_2 v_{2,eq} \tag{14}$$

where $\chi_1 = 0.47$ and $\chi_2 = 0.36$ and they are subject to uncertainties of $\pm 0.01$ and $\pm 0.06$, respectively. The expressions assuming affine network behavior for gels give similar $\chi$ parameter values ($\chi_1 = 0.48$ and $\chi_2 = 0.33$). Equation (14) indicates that $\chi$ of the PDMAAm – water system strongly depends on concentration. In an earlier work, Erman and Flory showed that when the $\chi$ parameter is expressed as a linear function of $v_{2,eq}$, a necessary condition for the non-ionic gels to go through critical conditions is to have $\chi_1 < 1/2$ and $\chi_2 > 1/3$.[47] Although the indicated requirements for the hydrogel collapse are rare for real polymer-solvent systems, Equation (14) shows that both these conditions are satisfied for the PDMAAm – water system. Thus, the present gel system is a suitable candidate for first order volume phase transition studies, which is, however, beyond the scope of the present paper.

### *Inhomogeneity of Gels*

Light scattering measurements were carried out on the hydrogels prepared in the range of $v_2^0$ between 0.03 and 0.30. Figure 7 shows the Rayleigh ratio $R(q)$ versus the scattering vector $q$ plots for PDMAAm hydrogels (filled symbols) and for the corresponding linear PDMAAm solutions (open symbols). The polymer concentrations $v_2^0$ are indicated in the Figure. In the range of $v_2^0 \leq 0.16$, the light

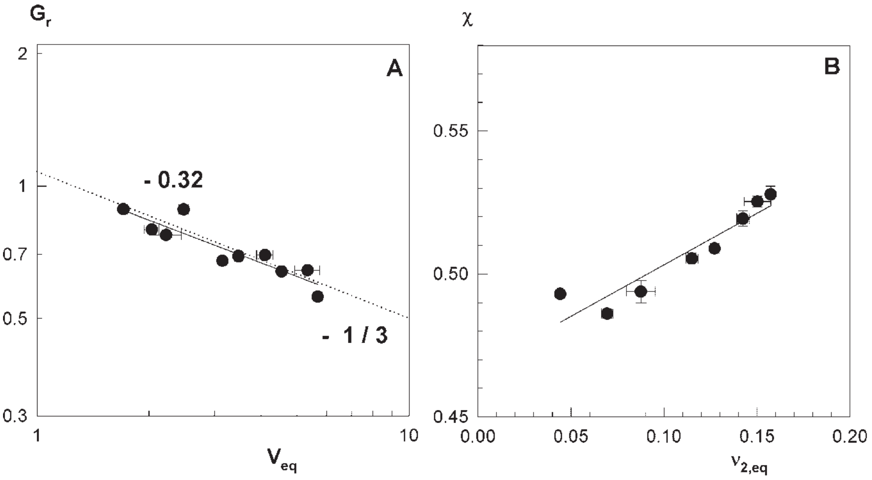

Figure 6. (A) Reduced modulus $G_r$, shown as a function of the normalized volume $V_{eq}$ of the equilibrium swollen gel. The solid curve is the best fit to the experimental data. The dotted curve represents the prediction of Equation (7). The corresponding slopes are shown. (B) $\chi$ parameter of PDMAAm-water system shown as a function of the concentration $\nu_{2,eq}$.

scattering intensity does not change much with the scattering vector $q$. However, at higher values of $\nu_2^0$, a marked curvature appears in the $R(q)$ vs. $q$ curves, especially at low angles. In this range of $\nu_2^0$, $R(q)$ of polymer solution even exceeds $R(q)$ of polymer gels. Due to the high polymer concentration in this regime, in addition to the concentration fluctuations, density fluctuations also play an important role in the scattering intensity, which seems to be responsible for the strong $q$-dependence of the Rayleigh ratios.[48] Figure 7 also shows that, for $\nu_2^0 \leq 0.16$, the scattering light intensity from polymer solutions decreases with increasing concentration $\nu_2^0$. Compared to solutions, the light scattering intensity from gels first increases slightly up to $\nu_2^0 = 0.06$ but then rapidly decreases.

Excess scattering intensities $R_{ex}(q)$ were calculated from the data points shown in Figure 7 as $R_{ex}(q) = R_{gel}(q) - R_{sol}(q)$, where $R_{gel}(q)$ and $R_{sol}(q)$ are the Rayleigh ratios for gel and polymer solution, respectively. To compare the excess scattering of different gels, we will focus on the scattering intensity measured at a fixed scattering vector $q = 1 \times 10^{-3}$ Å$^{-1}$. Figure 8A shows the scattering intensities from solutions $R_{sol,q}$ (open circles) and the excess scattering $R_{ex,q}$ (filled circles) at $q = 1 \times 10^{-3}$ Å$^{-1}$ plotted as a function of $\nu_2^0$. In Figure 8B, the ratio $R_{ex,q}/R_{gel,q}$, representing the contribution of the gel inhomogeneities to the scattering light intensity is plotted against $\nu_2^0$ by the symbols. The dotted curves in the Figures were calculated using the Panyukov-Rabin theory, as will be explained later.

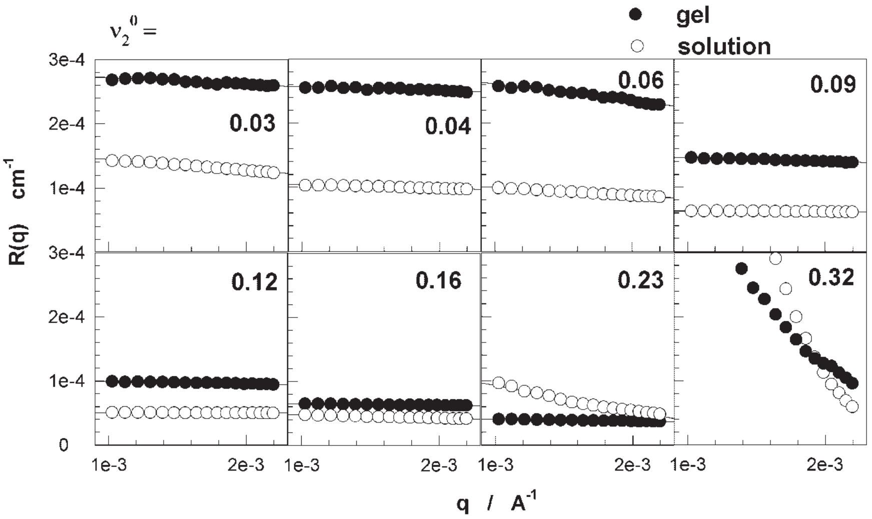

Figure 7. Rayleigh ratio $R(q)$ versus wave vector $q$ plots for the hydrogels (filled symbols) and for the corresponding linear polymer solutions (open symbols). The $\nu_2^0$ values are indicated in the Figure.

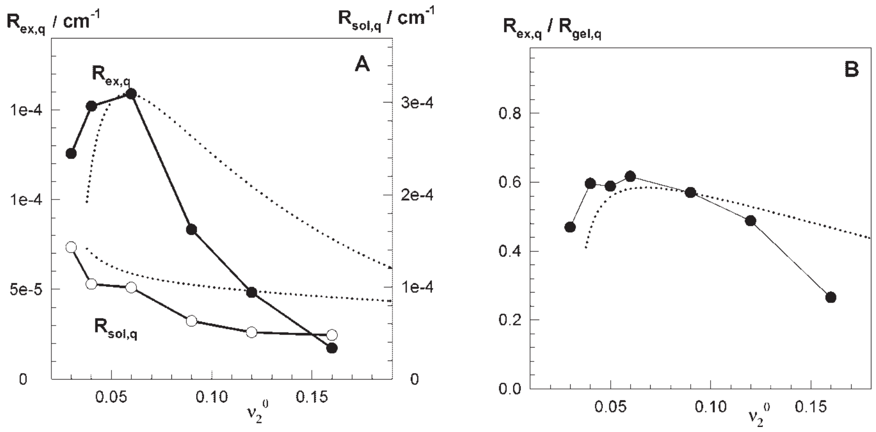

Figure 8. (A) Scattering intensity from solution $R_{sol,q}$ (open symbols) and excess scattering $R_{ex,q}$ from gels (filled symbols) measured at $q = 1 \times 10^{-3}$ Å$^{-1}$ shown as a function of $\nu_2^0$. (B) The $R_{ex,q}/R_{gel,q}$ ratio representing the fractional contribution of the gel inhomogeneities to the scattering light intensity at $q = 1 \times 10^{-3}$ Å$^{-1}$ shown as a function of $\nu_2^0$. The solid curves show the trend in the data. The dotted curves were calculated using the PR theory. The proportional constant $K'$ used in Figure 8B is $4.44 \times 10^{-4}$ cm$^{-1}$.

Figure 8A shows that, although the scattered light intensity from solution decreases with rising $\nu_2^0$, the excess scattering $R_{ex,q}$ first increases with $\nu_2^0$, but then decreases continuously. A maximum excess scattering in gels was observed at $\nu_2^0 = 0.06$. Since $R_{ex,q}$ is a measure of the spatial inhomogeneity in a gel, the results indicate that the PDMAAm gels formed at $\nu_2^0 = 0.06$ exhibit the highest degree of inhomogeneity. Such a maximum degree of spatial inhomogeneity at a critical polymer concentration was also observed recently in PAAm gels.[32] Figure 8B shows that the spatial inhomogeneity contributes 20 to 60% of the scattered light intensity from gels. The $R_{ex,q}/R_{gel,q}$ vs. $\nu_2^0$ dependence also exhibits a maximum at $\nu_2^0 = 0.06$.

Light scattering results from gels were first interpreted by the Debye-Bueche function:[33–36]

$$R_{ex}(q) = \frac{4\pi K \xi^3 \langle \eta^2 \rangle}{\left(1 + q^2 \xi^2\right)^2} \tag{15}$$

with $K$ being the optical constant, $K = 8\ \pi^2\ n^2\ \lambda^{-4}$, $\xi$ the correlation length of the scatterers and $\langle \eta^2 \rangle$ the mean square fluctuation of the refractive index. Note that $\xi$ is a characteristic length scale for gels and it corresponds to the size of the highly crosslinked regions. According to Equation (15), the slope and the intercept of $R_{ex}(q)^{-1/2}$ vs. $q^2$ plot (Debye-Bueche plot) give $\xi$ and $\langle \eta^2 \rangle$ of a gel sample. In Figure 9, the excess scattering data of gels are given in the form of Debye-Bueche plots. It can be seen that straight lines are obtained in this analysis. $\xi$ and $\langle \eta^2 \rangle$ values calculated from the Debye-Bueche analysis showed that, in the range $\nu_2^0 =$ 0.06 to 0.12, the correlation length of the scatterers remains almost constant at $\xi = 10 \pm 1$ nm, while the mean square fluctuations $\langle \eta^2 \rangle$ decrease slightly with increasing $\nu_2^0$ from $10 \times 10^{-7}$ up to $5 \times 10^{-7}$. It must be noted that the Debye-Bueche function gave negative slopes, both at very low and high values of $\nu_2^0$, so these parameters cannot be calculated. Although the narrow range of $q$ of light scattering experiments does not allow a definitive conclusion, the Debye-Bueche function assumes a two phase structure with a sharp boundary, which seems to be invalid at very low and high polymer concentrations.

Recently, Panyukov and Rabin (PR) proposed a statistical theory for describing the structure factor for gels formed by instantaneous crosslinking of semi-dilute polymer

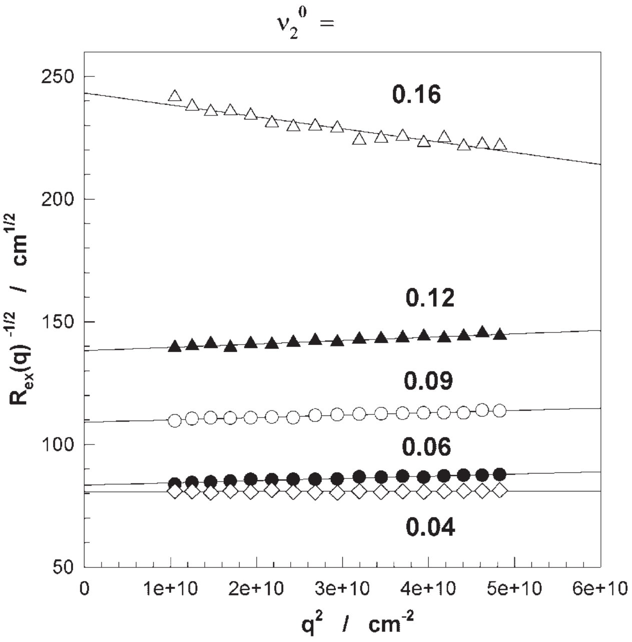

Figure 9. Debye-Bueche plots for the hydrogels prepared at various $\nu_2^0$ indicated in the Figure.

solutions.[39] In spite of the limitations in the applicability of the PR theory, it succeeded in predicting qualitatively the dependence of the spatial inhomogeneity in gels on the gel synthesis parameters.[24,25,32] The PR theory takes into account the effect of the network structure at preparation on the structure factor $S(q)$ under the conditions of the measurements. The structure factor of this theory consists of two contributions, one from the thermal fluctuations $G(q)$ and the other from the static inhomogeneities $C(q)$:

$$S(q) = G(q) + C(q) \tag{16}$$

Note that $G(q)$ is proportional to the scattering light intensity from the polymer solution $R_{\mathrm{sol}}(q)$, while $C(q)$ relates to the excess scattering $R_{\mathrm{ex}}(q)$. The measured scattered light intensity $R(q)$ relates to $S(q)$ by:

$$R(q) = K'S(q) \tag{16a}$$

where $K'$ is the proportional constant. $G(q)$ and $C(q)$ are given by the following equations:

$$G(q) = \frac{v_2 N g(q)}{1 + wg(q)} \tag{17}$$

$$C(q) = \frac{v_2 N}{(1 + wg(q))^2 (1 + Q^2)^2} \times \left(6 + \frac{9}{w_0 - 1 + 0.5Q^2 (v_2^0/v_2)^{2/3} (v_2^0)^{-1/4}}\right) \tag{18}$$

where $v_2$ is the volume fraction of crosslinked polymer in the gel at the measurement and $N$ is the number of segments between two successive crosslinks. $g(q)$ is the thermal correlator in the absence of the excluded volume effect,

$$g(q) = \frac{1}{0.5Q^2 + (4Q^2)^{-1} + 1} + \frac{2(v_2/v_2^0)^{2/3} (v_2^0)^{1/4}}{(1 + Q^2)^2} \tag{19}$$

$w$ and $w_0$ are the excluded volume parameters at the state of measurement and at gel preparation, respectively,

$$w = (1 - 2\chi + v_2) v_2 N \tag{20}$$

$$w_0 = (v_2^0)^{5/4} N \tag{21}$$

$Q$ is the reduced scattering vector normalized by the monomer fluctuating radius, $Q = a N^{1/2} q$, $a$ is the segment length, and the initial state of the gels is assumed to be in a good solvent (the scaling) regime while the final state is taken as a poor solvent (mean field) regime. Note that the number of segments per network chain $N$ is related to the effective crosslink density of the hydrogels $\nu_{\mathrm{e}}$ through the equation:

$$N = 1/(\nu_{\mathrm{e}} a^3 N_{\mathrm{A}}) \tag{22}$$

where $N_{\mathrm{A}}$ is Avogadro's number.

Theoretical prediction of the PR theory requires the network parameters at the state of the gel preparation as well as at the state of the measurements. For the present gels, $v_2$ is equal to $v_2^0$ because the light scattering measurements were conducted just after the gel preparation. Furthermore, the gel parameters $N$ and $\chi$ as a function of $v_2^0$ are available from the previous section. Non-linear curve fit to the experimental $\nu_{\mathrm{e}}$ vs. $v_2^0$ data given in Figure 5 give the following relation:

$$\nu_{\mathrm{e}}/(\mathrm{mol} \cdot \mathrm{m}^{-3}) = -69 + 2389 v_2^0 - 5389 (v_2^0)^2 + 3610 (v_2^0)^3 \quad \text{for } v_2^0 < 0.7 \tag{23}$$

which was used, together with Equation (22), for the calculation of $N$ vs. $v_2^0$ dependence. The concentration dependent $\chi$ parameter of the present gel system was given by Equation (14). The segment length $a$ was evaluated by fitting $C_q/S_q$ ratio of the theory at $q = 1 \times 10^{-3}$ Å$^{-1}$ to the experimental $R_{\mathrm{ex},q}/R_{\mathrm{gel},q}$ data of the hydrogels. Taking $a$ as a fit parameter, the sum of the squared residuals between $C_q/S_q$ and $R_{\mathrm{ex},q}/R_{\mathrm{gel},q}$ was minimized. The dotted curve in Figure 8B, which is the best fit to the experimental $R_{\mathrm{ex},q}/R_{\mathrm{gel},q}$ data yielded $a = 3.4$ Å. This value is comparable with the bond length of vinyl monomers but about three fold smaller than the statistical segment length of acrylamide polymers. The proportional constant $K'$ was taken as a vertical shift factor for the structure factor $S(q)$.

In Figure 8A, the dotted curves show $R_{\mathrm{ex},q}$ and $R_{\mathrm{sol},q}$ vs. $v_2^0$ dependences of the theory. Comparison of the experimental results with the theoretical curves shows that PR theory qualitatively predicts the behavior of PDMAAm gels. $R_{\mathrm{ex},q}$ first increase with increasing $v_2^0$, reaching a maximum at $v_2^0 = 0.06$, then they decrease continuously with a further increase in $v_2^0$.

Assuming that the effective crosslink density $\nu_{\mathrm{e}}$ of the gels remains constant over the entire range of $v_2^0$, one may expect a continuous decrease of the gel inhomogeneity with rising $v_2^0$. This is due to the fact that increasing the polymer concentration progressively reduces the concentration fluctuations between the densely and loosely crosslinked regions of the gels. Indeed, calculations using the PR theory for a fixed $\nu_{\mathrm{e}}$ but varying $v_2^0$ predict a continuous decrease in both $C_q$ and $C_q/S_q$ with increasing $v_2^0$.

However, as can be seen in Figure 5, the crosslink density $\nu_{\mathrm{e}}$ is not a constant, but increases with $v_2^0$ in the first regime, which is the range of the light scattering measurements. Since the spatial inhomogeneity becomes larger on raising the crosslink density, a second effect of increasing $v_2^0$ is to enhance the gel inhomogeneity. The dependence of the excess scattering on the monomer concentration is thus determined by competition between two opposite effects. At $v_2^0 < 0.06$, the crosslink density effect dominates over the concentration effect so that the gel inhomogeneity increases with $v_2^0$. At $v_2^0 > 0.06$, the concentration effect is more dominant than the crosslink density effect so that the gel inhomogeneity decreases with $v_2^0$.

## Conclusions

The equilibrium swelling degree, modulus of elasticity and the spatial inhomogeneity of PDMAAm hydrogels were investigated at a fixed crosslinker ratio but over the entire range of the initial monomer concentration. Both the linear swelling ratio of gels $D/D_0$ and the polymer volume fraction in the equilibrium swollen gel $v_{2,\mathrm{eq}}$ were found to increase with increasing polymer concentration after the gel preparation $v_2^0$. Depending on the value of $v_2^0$, three different gel regimes were observed: (1) For $v_2^0 < 0.3$, increasing $v_2^0$ decreases the extent of cyclization reactions during the gel formation process so that the effective crosslink density of gels increases with rising $v_2^0$. (2) For $0.3 < v_2^0 < 0.7$, increasing $v_2^0$ reduces the accessibility of the pendant vinyl groups during crosslinking due to the steric hindrance at high polymer concentrations. As a result, the effective crosslink density of gels decreases with increasing $v_2^0$. (3) For $v_2^0 > 0.7$, the modulus of elasticity increases sharply with increasing $v_2^0$ due to the increasing extent of chain entanglements. Static light scattering measurements on gels show that the degree of spatial gel inhomogeneity in PDMAAm gels attains a maximum value at $v_2^0 = 0.06$. The appearance of a maximum as well as $v_2^0$-dependence of scattered light intensities from gels were successfully reproduced by the theory proposed by Panyukov and Rabin.

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