6558 *Macromolecules* **2004,** *37,* 6558−6564

Influence of Formation Conditions on Spatial Inhomogeneities in Poly(*N*-isopropylacrylamide) Hydrogels

Jingjing Nie, Binyang Du, and Wilhelm Oppermann*

Institute of Physical Chemistry, Technical University of Clausthal, Arnold-Sommerfeld Strasse 4, 38678 Clausthal-Zellerfeld, Germany

Received April 28, 2004; Revised Manuscript Received June 24, 2004

ABSTRACT: Static light scattering measurements performed on poly(*N*-isopropylacrylamide) hydrogels having a polymer volume fraction around 0.05−0.09 reveal that spatial inhomogeneities grow stronger with rising preparation temperature of the gels, increasing cross-linker concentration, and decreasing monomer concentration. Quantitative analysis of the angular dependence of the excess scattering intensity via the Debye−Bueche method results in correlation lengths of several 10 nm. Relative mean-square concentration fluctuations on this length scale are around 15−35% depending on preparation conditions. The cross-linking efficiency as determined by shear modulus measurements declines when the degree of inhomogeneity is enhanced. Comparison of the experimental results with Panyukov−Rabin (PR) theory indicates that the general trends are well predicted and that thermal concentration fluctuations can be calculated almost quantitatively. However, the theory significantly underestimates the static spatial concentration fluctuations. This discrepancy may be a consequence of preparing the gels by cross-linking polymerization, which leads to much stronger heterogeneity than presumed in PR theory.

Introduction

Networks, in particular hydrogels, made by free-radical cross-linking copolymerization have received much attention in the last years due to both scientific and technological importance. Their static and dynamic properties on macroscopic as well as on microscopic length scales are far more complicated than those of corresponding polymer solutions. This is due to the characteristic topological connectivity of network chains. Predominantly at the beginning of the polymerization, extensive cyclization and multiple cross-linking reactions take place leading to rather compact clusters or microgel particles in the pregel state.[1−3] As the reaction proceeds to higher conversion, gelation occurs by interconnecting these objects to form a continuous network. To model such reactions, kinetic theories as well as computer simulations have been put forward.[4−6] Major consequences of this scheme are fairly low cross-linking efficiency, rather high gel-point conversion, and structural inhomogeneity on the length scale of the primary clusters. These structural inhomogeneities are expected to affect the macroscopic physical properties of the gels, such as mechanical and swelling properties. Understanding and controlling the structural inhomogeneities of hydrogels has been a challenge in polymer science for decades.

Since the structural inhomogeneities of hydrogels are mainly dependent on how the gel was formed, it is important to theoretically and experimentally study the effect of formation conditions, specified e.g. by type of cross-linker (reactivity, functionality), concentrations of cross-linker and monomer, solvent quality, etc. A convenient way to probe structural inhomogeneities is by scattering methods. The network inhomogeneity is often characterized by the excess scattering intensity, namely the difference of the scattering of the gel and that of the corresponding semidilute solution. For example, Geissler, Horkay, and their coauthors investigated the scattering and swelling properties of inhomogeneous polyacrylamide (PAAm) hydrogels by dynamic light scattering and small-angle X-ray scattering techniques and showed how the osmotic and elastic properties of the networks were influenced by structural inhomogeneities.[7] They also investigated the structures of poly(vinyl alcohol) hydrogels and obtained similar results for the thermodynamically fluctuating part of the scattering intensity by dynamic and static light scattering, as well as by small-angle neutron scattering measurements, respectively.[8] Shibayama et al.[9−15] have extensively studied the structure and dynamics of PAAm and poly(*N*-isopropylacrylamide) (PNIPA) gels prepared at various conditions by small-angle neutron scattering and dynamic light scattering. In the dynamic light scattering measurements, they successfully described the diffusion coefficient and the scattered intensity component from the thermodynamic fluctuation by employing the partial heterodyne method. Lindemann et al.[16] employed static light scattering to study the influence of cross-linker reactivity on the formation of inhomogeneities in PAAm hydrogels and related this to cross-linking efficiency. Kizilay and Okay[17] focused on the effect of initial monomer concentration on spatial inhomogeneity in PAAm gels by static light scattering. They observed a critical monomer concentration where the degree of the inhomogeneity of PAAm gels attained a maximum value. A considerable selection of the available static scattering data was reviewed by Bastide and Candeau.[18] Moreover, the progress in investigating the spatial inhomogeneity and dynamic fluctuations of polymer gels was reviewed by Shibayama.[19]

On the theoretical side, a few years ago Panyukov and Rabin[20] presented a phenomenological theory of randomly cross-linked polymer networks. They derived expressions to describe the structure factor of polymer gels valid for the entire range of wavelengths up to continuum length scales, which can be directly mea-

---

* To whom correspondence should be addressed. E-mail: wilhelm.oppermann@tu-clausthal.de.

10.1021/ma049169d CCC: $27.50

Table 1. Experimental Conditions and Relevant Results

C_{NIPA} (mM)	C_{BIS} (mM)	T_{prep} (°C)	ϕ_0 (%)	G_0 (kPa)	ν_{eff} (mol/m^3)	N	ξ (nm)	$10^6\langle\eta^2\rangle$
549	16.1	25.0	5.57	1.30	18.8	520	20	11
646	16.1	25.0	6.56	1.90	23.4	420	21	8.0
743	16.1	25.0	7.54	2.54	27.2	360	18	5.7
834	16.1	25.0	8.47	2.88	27.5	360	14	5.4
646	*7.9*	25.0	6.56	0.76	9.4	1050	12	2.8
646	**10.6**	25.0	6.56	1.23	15.2	650	13	4.9
646	**12.5**	25.0	6.56	1.33	16.4	600	18	6.2
646	**16.1**	25.0	6.56	1.90	23.4	420	21	8.0
646	16.1	**20.0**	6.56	3.00	37.6	260	16	5.2
646	16.1	**22.5**	6.56	2.45	30.4	320	18	6.0
646	16.1	**25.0**	6.56	1.90	23.4	420	21	8.0
646	16.1	**27.5**	6.56	1.70	20.8	470	29	18
646	16.1	**30.0**	6.56	0.82	9.9	990		

sured in static neutron and light scattering experiments. Panyukov and Rabin theory (PR theory) has been used successfully to fit qualitatively the experimental results of small-angle neutron scattering[14,15] and static light scattering.[17]

Static inhomogeneities dominate the scattering from a gel at long wavelengths; hence, light scattering measurements are well suited to probe this regime. In this work, we systematically investigate the influence of formation conditions on the spatial inhomogeneities in PNIPA hydrogels (by static light scattering) and on their mechanical properties (by shear modulus measurements). Emphasis is placed on a variation of several parameters under comparable conditions. We also compare our experimental results to PR theory to theoretically elucidate the effect of formation conditions on the spatial inhomogeneity in hydrogels.

Experimental Section

Sample Preparation. *N*-Isopropylacrylamide (NIPA, ACROS), *N*,*N*′-methylenebis(acrylamide) (BIS, Sigma), potassium peroxodisulfate ($K_2S_2O_8$, Sigma), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Sigma) were used as received. PNIPA hydrogels were prepared by free-radical cross-linking copolymerization of NIPA and BIS in an aqueous solution in the presence of 1.6 mM $K_2S_2O_8$ initiator and 5.4 mM TEMED accelerator. Corresponding polymer solutions were obtained by free-radical polymerization under identical conditions but omitting BIS. Three series of gels and solutions were prepared by changing the initial concentration of NIPA (C_{NIPA}), the concentration of BIS (C_{BIS}), or the preparation temperature (T_{prep}), respectively. Temperature control was achieved by a water bath. The solutions and the gel samples were prepared in the light scattering vials having 8 mm inner diameter. Dust was removed from the solutions by filtering them through Nylon membrane filters of 0.2 μm pore size. Details about the synthesis conditions are listed in Table 1.

Mechanical Measurements. The shear moduli of the gels were measured by a stress-controlled mechanical rheometer (CVO Rheometer, Bohlin Instruments) with the geometry of parallel plates of 40 mm diameter. To avoid the additional errors of measurements by treating and transferring samples after the preparation of the gels, PNIPA gels were directly polymerized between the parallel plates. To overcome the evaporation of water, a cover was used, which is sealed with water, to fit a solvent trap to the measuring system. The polymerization process was in-situ monitored by measuring the storage modulus G' and the loss modulus G'' of the system at 1 Hz as a function of time. Both moduli reached plateau values after several hours, indicating completion of the polymerization. Frequency sweeps showed that G' obtained at 1 Hz was identical with the equilibrium modulus within experimental error.

Static Light Scattering Measurements. Static light scattering measurements were performed at 25 °C in the angular range 50−140° using a goniometer SLS-2 equipped with a He−Ne laser (λ = 632.8 nm). The absolute intensity was calibrated against a toluene standard. To obtain correct spatial averaging, six measurements at different positions achieved by a 60° rotation of the vial between successive measurements were made. The excess scattering of the gel was determined by measuring the total scattering intensity of the gel and subtracting the scattering intensity of an un-cross-linked sample of the same polymer concentration.

Results and Discussion

The physical properties of gels are mainly dependent on the network density and the structure development of the network during the gelation process. The network density ν_{th} of an ideal network whose network chains between cross-links are all elastically effective can be calculated from the molar concentration of the cross-linker C_{BIS} in the system by assuming that all cross-linker molecules had completely reacted as tetrafunctional junction points: $\nu_{\mathrm{th}} = 2C_{\mathrm{BIS}}/\phi_0$. This defines a reference state of the network. In fact, the cross-linkers may not have completely reacted and the real network may contain a variety of defects, a wide distribution of chain lengths between junction points, and inhomogeneities of cross-link density and connectivity. The macroscopic physical properties of real gels, such as swelling behavior and elasticity, are dominated by the effective network density ν_{eff}. For a network of Gaussian chains, the effective network density ν_{eff} is related to the shear modulus G_0 measured in the state of gel preparation by[21,22]

$$G_0 = A\nu_{\mathrm{eff}}RT\phi_0 \tag{1}$$

The ratio $\nu_{\mathrm{eff}}/\nu_{\mathrm{th}}$ (cross-linking efficiency) can serve as a measure for the extent of nonideality. In eq 1 the structure factor A equals 1 for an affine network and $1 - 2/f$ for a phantom network, f being the functionality of the cross-links. R is the gas constant, T the absolute temperature, and ϕ_0 the polymer volume fraction at sample preparation. Swollen networks are generally considered as phantom networks; hence, $A = 0.5$ in the case of tetrafunctional cross-links. ϕ_0 can be calculated from the initial molar concentration of the monomers as $\phi_0 = C_{\mathrm{NIPA}}\bar{V}$, where $\bar{V} = 101.5$ mL/mol is the molar volume of PNIPA repeat units (the molar mass of a repeat unit is 113.2 g/mol, and the density of NIPA is 1.115 g/cm^3).[23] The effective average number of segments between two successive cross-links, N, is then given by

$$N = \frac{1}{\nu_{\mathrm{eff}}\bar{V}} \tag{2}$$

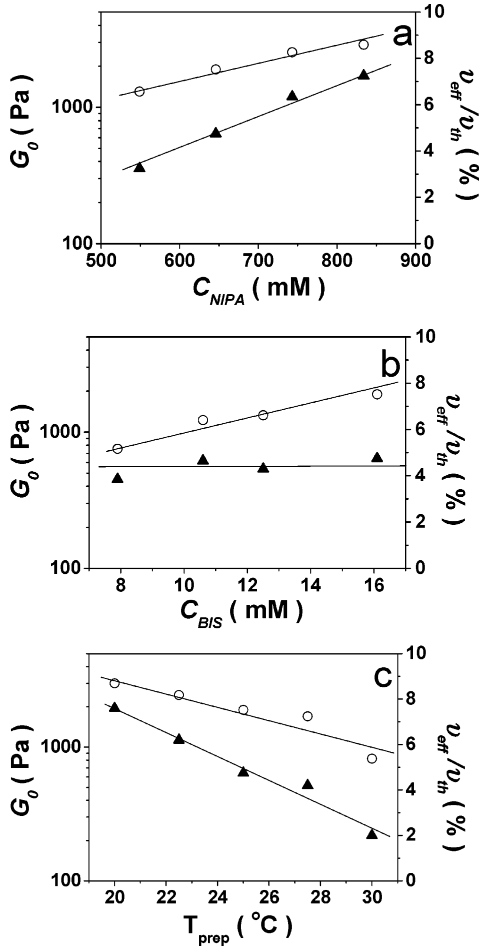

Figure 1. Elastic modulus G_0 (○) and the cross-linking efficiency ν_{eff}/ν_{th} (▲) of PNIPA gels prepared at different monomer concentrations, C_{NIPA} (a), cross-linker concentrations, C_{BIS} (b), and preparation temperatures, T_{prep} (c). The lines were drawn for the eye.

The shear modulus G_0 of gels measured in the state of sample preparation, the calculated effective network density ν_{eff}, and the number of segments between cross-links N are summarized in Table 1 for different preparation conditions.

Figure 1 shows the shear modulus G_0 and cross-linking efficiency ν_{eff}/ν_{th} of the three series of gels as a function of preparation temperature (T_{prep}), concentration of cross-linker (C_{BIS}), and monomer (C_{NIPA}), respectively. Note that all of the cross-linking efficiencies are less than 10% at all preparation conditions applied in this study, indicating the nonidealities of the cross-linking reaction such as cyclization, multiple cross-linking, and cross-link agglomerations. When the concentration of cross-linker is fixed, the cross-linking efficiency increases with rising monomer concentration (Figure 1a). This is a consequence of the decreasing probability of cyclization and multiple cross-linking reactions. Interestingly, the cross-linking efficiency is almost independent of the concentration of cross-linker when the concentration of monomer is fixed (Figure 1b). This result differs from the system of poly(acrylamide) (PAAm) gels, where the cross-linking efficiency decreases as the concentration of cross-linker is increased.[17] It seems that for neutral PINPA gel the increase of cross-linker concentration will increase the probability of cross-linking and nonideal reaction to the same extent, while for weakly charged PAAm gel, the increasing probability of nonideal reaction is larger than that of cross-linking. When both the concentration of cross-linker and monomer are fixed, the cross-linking efficiency decreases markedly with increasing preparation temperature of the gels (Figure 1c). Since PNIPA exhibits a lower critical solution temperature (LCST) of ~32−34 °C,[24,25] increasing the preparation temperature is likely to raise the probability of cyclization and other inefficient cross-linking reactions. Microgels formed in intermediate states of the cross-linking polymerization are less swollen at higher temperatures, and thus a greater extent of reaction is required to achieve a continuously interconnected gel. Sayil and Okay have also reported that the cross-linking efficiency is a decreasing function of the preparation temperature by studying the swelling behavior of PNIPA gels as a function of preparation temperature. They state that a macroscopic network of interconnected clusters was formed when the preparation temperature is higher than 20 °C, which decreases the effective cross-link density of the gels.[26]

To investigate the effects of preparation conditions on the microstructure of PNIPA hydrogels, static light scattering experiments were carried out at a constant temperature of 25 °C for all of the samples except for the one prepared at 30 °C, which is opaque and cannot be measured. The scattered light intensities were recorded from 50 to 140°, which corresponds to a scattering vector range of $q = 1.1 \times 10^{-3}$−2.5×10^{-3} Å^{-1}, where $q = (4\pi n/\lambda)\sin(\theta/2)$ with θ, λ, and n being the scattering angle, the wavelength of the incident light in a vacuum, and the refractive index of the medium, respectively. Figure 2 shows the Rayleigh ratio $R(q)$ vs the square of the scattering vector q^2 for PNIPA gels prepared under different conditions and for the corresponding solutions of linear PNIPA.

First of all, it is noteworthy that the scattering intensity of the linear PNIPA solutions measured at 25 °C is independent of the preparation temperature (Figure 2c, open symbols). This reflects the fact that measurements on solutions probe thermodynamically controlled concentration fluctuations, which are determined by the conditions (temperature) where the measurement is made. It also shows that changing the preparation temperature has no drastic effect on the polymerization reaction itself. The dependence of the scattering intensity on concentration is also very weak (Figure 2a, open symbols). This is due to the fact that we are in the semidilute regime.

The scattering intensity of the gels is generally more than 10 times higher than that of the corresponding solutions and varies as a function of monomer concentration, cross-linker concentration, and preparation temperature. In particular, the scattering intensity of hydrogels increases markedly with increasing the preparation temperature. The closer the preparation temperature is to the phase transition temperature, the more the structure of the gel is affected. As we observe from Figure 2c, increasing the preparation temperature from 20.0 to 22.5 °C only leads to a small increase in the scattering intensity, whereas it rises drastically by a factor of 4 when the preparation temperature is changed from 25.0 to 27.5 °C.

Generally, the scattering intensity of a gel, $R_{gel}(q)$, is assumed to be due to the sum of thermal concentration fluctuations (ergodic contribution) and of static spatial

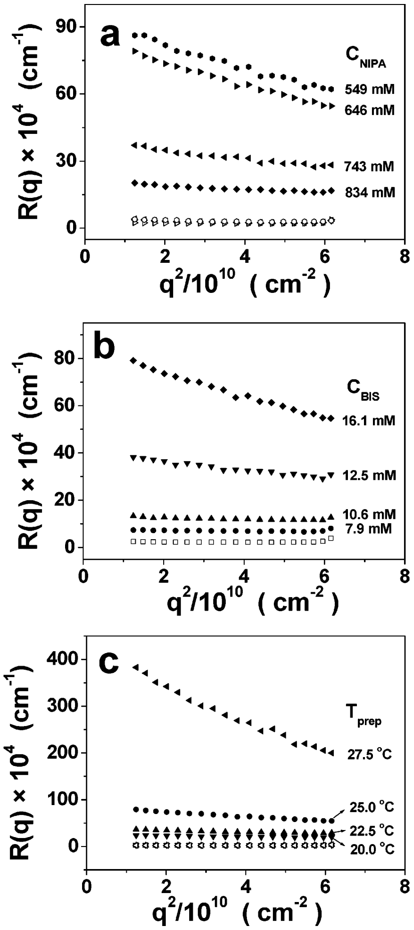

Figure 2. Rayleigh ratio $R(q)$ vs q^2 of PNIPA gels prepared at different monomer concentrations, C_{NIPA} (a), cross-linker concentrations, C_{BIS} (b), and preparation temperatures, T_{prep} (c). The solid and open symbols present the Rayleigh ratio $R(q)$ of PNIPA gels and that of the corresponding linear PNIPA solutions, respectively.

inhomogeneities resulting from the cross-linking process (nonergodic contribution). The latter is of interest to characterize the microstructure of gels. In an experimental approach to determine this quantity one presumes that the thermal fluctuations in a gel are practically identical with those in a solution of the linear polymer; hence

$$R_{gel}(q) = R_{sol}(q) + R_{ex}(q) \quad (3)$$

This procedure is justified when the scattering of the gel exceeds by far that of the solution, as is the case in this study.

Extensive dynamic light scattering studies on PNIPA hydrogels show that the dynamic fluctuations in these gels depend neither on the cross-link density nor the preparation temperature of the gels, while the static inhomogeneities of the gels rise with increasing of the cross-linker concentration and the preparation temperature of the gels.[10] The unchanged scattering intensity of solutions of the linear PNIPA may indicate that the dynamic fluctuations of PNIPA gels are independent of monomer concentration and preparation temperature.

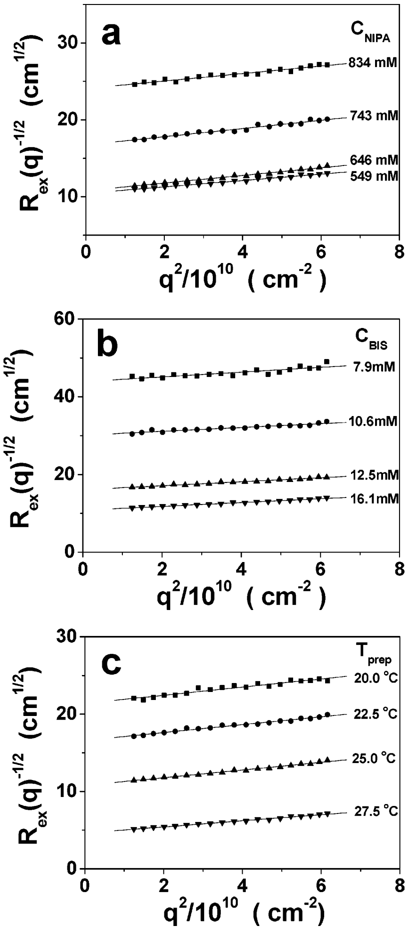

Figure 3. Debye–Bueche plots $R_{ex}(q)^{-1/2}$ vs q^2 of PNIPA gels as a function of (a) monomer concentration, C_{NIPA}, (b) cross-linker concentration, C_{BIS}, and (c) preparation temperature, T_{prep}.

By analysis of the excess scattering $R_{ex}(q)$ of gels with the Debye–Bueche method,[27–30] the correlation length ξ and the mean square refractive index fluctuation $\langle\eta^2\rangle$ of gels, which are widely used to characterize the network structures and inhomogeneities of gels, can be obtained. The excess scattering $R_{ex}(q)$ is given by

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

where $K = 8\pi^2n^2\lambda^{-4}$. Data are commonly fitted to eq 4 by plotting $R_{ex}(q)^{-1/2}$ vs q^2 (Debye–Bueche plot) to obtain straight lines. Figure 3 shows such plots for the same data as in Figure 2. It can be seen that this type of analysis works pretty well. From the slope and intercept of these $R_{ex}(q)^{-1/2}$ vs q^2 plots, the correlation length ξ and the mean square refractive index fluctuation $\langle\eta^2\rangle$ of PNIPA hydrogels were determined and included in Table 1. The correlation lengths are of the order of several 10 nm. The mean-square refractive index fluctuation is in the range $(3-18) \times 10^{-6}$. With the refractive index increment of PNIPA in water at 25 °C,[31] $dn/dc = 0.167$ mL/g, this translates into static concentration fluctuations $\sqrt{\langle\delta\phi^2\rangle} \approx 0.01-0.025$. Since the mean volume fraction of polymer in the gels, ϕ_0, is around 0.07, the average relative static concentration fluctuation on a lengths scale of 10 nm is quite large around 15–35%. In other words, the gels are highly inhomogeneous. This explains the fact that the cross-linking efficiencies are so low and links macroscopic properties to microstructural features.

More detailed inspection of the data reveals that both ξ and $\langle\eta^2\rangle$ increase with decreasing monomer concentration and with rising preparation temperature, when the concentration of cross-linker is fixed. The latter observation agrees with results obtained by Shibayama using dynamic light scattering.[10] Norisuye et al.[14] found that the swelling ratio of PNIPA gels made by cross-linking copolymerization increased significantly with the preparation temperature, indicating that more and more congregation of cross-links occurs as the temperature rises. This increase of inhomogeneity of PNIPA gels with increasing preparation temperature was further confirmed by dynamic light scattering experiments. The decrease of monomer concentration and the increase of preparation temperature both lead to lowering the cross-linking efficiency as shown above by the shear modulus measurements. It is apparent that the lower cross-linking efficiency is coupled to a higher degree of inhomogeneity (at constant cross-linker concentration).

Furthermore, both ξ and $\langle\eta^2\rangle$ of the PNIPA hydrogels increase with increasing the concentration of cross-linker, when the monomer concentration and the preparation temperature are fixed. Again, the results from static light scattering are consistent with those obtained by shear modulus measurements, which shows that increasing the concentration of the cross-linker increases the effective network density and the inhomogeneities of the gels at the same time, leading to the unchanged cross-linking efficiency. Our results also indicate that increasing the ratio of cross-linker to monomer increases the inhomogeneities of PNIPA gels. These results are in agreement with a small-angle neutron scattering study of the same system, where it was found that the inhomogeneity correlation length increased with the increase of cross-linker concentration and the preparation temperature when the concentration of monomer was fixed.[15]

Recently, Panyukov and Rabin proposed a phenomenological theory (PR theory) to describe the network structure of randomly cross-linked polymer gels.[20] It is based on the separation of solidlike and liquidlike degrees of freedom and takes into account the frozen inhomogeneities due to cross-linking. An expression for the structure factor $S(q)$ of polymer gels is given, i.e., the density correlation function, which can be obtained by static scattering experiments. The validity of PR theory has been tested by comparison with the experimental results of small-angle neutron scattering[14,15] and static light scattering.[17]

Here, we try to compare PR theory with our results of static light scattering experiments on PNIPA hydrogels prepared at different conditions. Before doing so, it needs to be mentioned that PR theory proceeds from the assumption that the network is prepared with only small degrees of frozen disorder (network formation should have taken place in a good solvent away from the cross-link saturation threshold). This is not generally the case for the gels considered in this work. In fact it was aimed at generating more pronounced network inhomogeneity by approaching the LCST during preparation of the gels. Consequently, PR theory can give some guideline, but quantitative agreement should not be expected.

Two alternatives were considered by PR for the performance of the scattering experiments: in good solvent conditions or in Θ conditions. A good solvent in PR theory is an *athermal* solvent, where the Flory interaction parameter $\chi = 0$, while Θ-solvent conditions corresponds to $\chi = 0.5$. The formulas derived for these two cases have both been used for a comparison with the experimental results. Takata et al.[15] applied the theory for good solvents to gels of poly(*N*-isopropyl acrylamide) in water, which were prepared at different temperatures in the range 10−27 °C and studied at 20 °C by small-angle neutron scattering. Kizilay and Okay[17] used the Θ-conditions approach for light scattering data obtained on aqueous poly(acrylamide) gels at 24 °C with $\chi = 0.481$.

According to PR theory,[20] the structure factor of the polymer gels $S(q)$ includes a contribution from thermal density fluctuations $G(q)$ (thermal correlator) and one from static density inhomogeneities $C(q)$ (static correlator):

$$S(q) = G(q) + C(q) \tag{5}$$

Here

$$G(q) = \frac{a^{-3}\phi N g(q)}{1 + w g(q)} \tag{6}$$

$$C(q) = \frac{a^{-3}\phi N}{(1 + w g(q))^2 (1 + Q^2)^2} \times \left(6 + \frac{9}{w_0 - 1 + 0.5Q^2(\phi_0/\phi)^{5/12}}\right) \tag{7}$$

where a is the statistical segment length and N the number of segments between two successive cross-links (see eq 2). ϕ and ϕ_0 are the volume fraction of polymer gel at the states of measurement and preparation, respectively. Q is defined as a dimensionless wave vector by $Q = aN^{1/2}q$. The dimensionless function $g(q)$ is given by

$$g(q) = \frac{1}{0.5Q^2 + (4Q^2)^{-1} + 1} + \frac{2(\phi/\phi_0)^{2/3}\phi_0^{1/4}}{(1 + Q^2)^2} \tag{8}$$

The dimensionless quantities w and w_0 are the effective virial coefficients in the state of measurement and preparation, respectively. In good-solvent conditions

$$w = \phi^{5/4}N, \quad w_0 = \phi_0^{5/4}N \tag{9}$$

while in a Θ-solvent

$$w = \phi^2 N \tag{10}$$

(PR considers network formation in good solvent only.)

To calculate the theoretical structure factor $S(q)$ of polymer gels with above equations, one needs to know the segment length a, the average number of segments N between two successive cross-links, and the volume fraction of polymer in the states of measurement and preparation, ϕ and ϕ_0. Furthermore, it has to be decided whether good-solvent or Θ-solvent conditions are to be applied.

In our case, scattering measurements were made at the same volume fraction as used for preparation of the networks; hence $\phi/\phi_0 = 1$. N is calculated from the measured shear modulus via eqs 1 and 2, and the corresponding data are listed in Table 1. The segment length a was set to 8.12 Å, as calculated from the characteristic ratio of 10.6 for PNIPA assuming that the number of segments N is identical with the number of monomers.[32] (This definition of the statistical segment

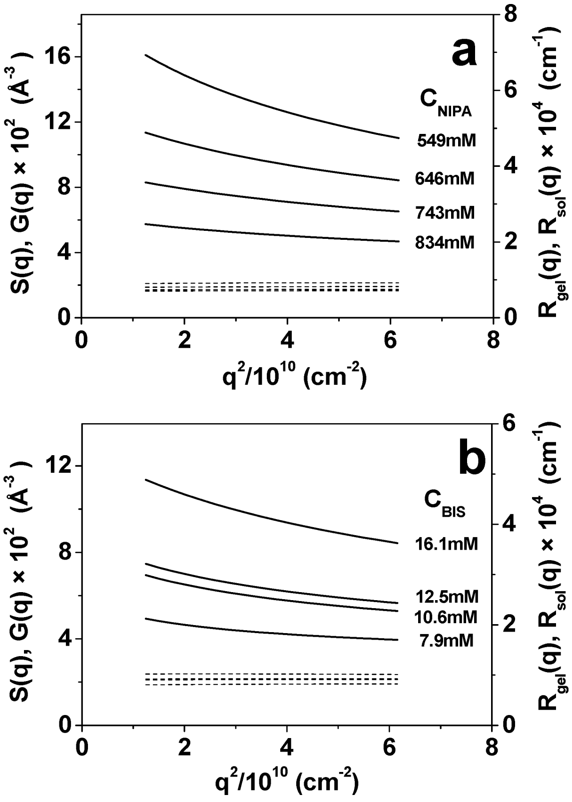

Figure 4. Theoretical calculated structure factor $S(q)$ (solid lines) and $G(q)$ (broken lines) of PNIPA gels and their corresponding Rayleigh ratio $R_{\mathrm{gel}}(q)$ (solid lines) and $R_{\mathrm{sol}}(q)$ (broken lines) as a function of (a) monomer concentration, C_{NIPA}, and (b) cross-linker concentration, C_{BIS}.

length deviates from the usual one based on the equivalent freely jointed chain;[33] it is, however, corresponding to other literature.[34])

Poly(N-isopropyl acrylamide) in water has a Θ temperature around 31 °C meaning that $\chi(31\ °\mathrm{C}) \approx 0.5$.[35] At 25 °C, where most of our measurements were made, the solvent quality is somewhat better and $\chi(25\ °\mathrm{C}) \approx 0.42$ was reported.[15] In our view, this is still fairly close to Θ conditions and justifies the use of eq 10 to obtain an estimate of the virial coefficient w. Contrary to PR's original paper, we assume $w_0 = w = \phi^2 N$ as well, because the networks were prepared under the same bad-solvent conditions, namely at 25 °C. (We do not attempt to make a calculation for samples synthesized at different temperatures, because this would require detailed information on χ(T) or w(T), respectively. Some authors used the relationship $w = (1 - 2\chi + \phi)\phi N$ to account for intermediate solvent quality.[14,15] As pointed out above, PR theory rests on the assumption that the network is prepared in an athermal solvent. Since this requirement is not fulfilled, the calculations can only give approximate results. Therefore, we prefer to keep the number of parameters to a minimum and refrain from using χ as an additional input quantity.)

Using eq 5−8 and 10, the theoretical structure factors $S(q)$, $G(q)$, and $C(q)$ of PNIPA gels were calculated. Figure 4a,b shows the calculated $S(q)$ (solid lines) and $G(q)$ (broken lines) as a function of monomer concentration and cross-linker concentration. It is seen that $S(q)$ predicted by PR theory increases with decreasing monomer concentration when the concentration of cross-linker is fixed (Figure 4a). Furthermore, $S(q)$ calculated by PR theory increases with rising cross-linker concentration when the concentration of monomer is held constant (Figure 4b). Clearly, the theoretical calculations show the same tendency as the experimental results (Figure 2a,b). The calculated $G(q)$ is almost independent of monomer concentration or cross-linker concentration, which is also consistent with the experimental findings on solutions.

For a more stringent comparison between theory and experiment, absolute scattering intensities should be considered. The calculated structure factor, $S(q)$, can be directly converted into the Rayleigh ratio $R(q)$ by[36]

$$R(q) = b^2 S(q) \tag{11}$$

where b is the scattering length of the segment, in light scattering experiments, given by

$$b = \frac{2\pi n M_{\mathrm{m}}}{N_{\mathrm{A}}\lambda^2}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right) \tag{12}$$

Here dn/dc is the refractive index increment. As an estimate we assume that the low concentration value of 0.167 mL/g reported[31] for PNIPA in water at 25 °C applies in concentrated systems a well. M_{m} is the molecular weight of the segment. Since we equate segments and monomers (when counting the number of segments between cross-links, N), the molecular weight of the monomer of 113.2 g/mol can be used. N_{A} is Avogadro's constant, λ the wavelength of the incident light in a vacuum, and n the refractive index of the medium.

The calculated Rayleigh ratios $R_{\mathrm{gel}}(q)$ (obtained from $S(q)$) and $R_{\mathrm{sol}}(q)$ (obtained from $G(q)$) are shown on the right axis in Figure 4. A quantitative comparison is now possible with the experimental data shown in Figure 2. The calculated $R_{\mathrm{sol}}(q)$ attributed to thermal density fluctuations of the gels is well in the order of magnitude of the Rayleigh ratio measured for the solutions of linear poly-NIPA (10^{-4} cm^{-1}). However, the calculated Rayleigh ratio $R_{\mathrm{gel}}(q)$ of the gels is about 10 times smaller than the experimental results.

To discuss this discrepancy, it is pertinent to have a closer look on the parameters (ϕ, N, a) and assumptions where the calculations are based upon. ϕ or ϕ_0 is fairly accurate. The quantity N is determined by modulus measurements whose results show some scatter in the order of ±15% (cf. Figure 1). This includes variations due to the synthesis of the gels. The fact that the spacing between some of the curves in Figures 2 and 4 appears somewhat erratic can be traced back to the uncertainty in N. However, this uncertainty cannot account for the order of magnitude discrepancy between theory and experiment. The correct value of the segment length, a, is crucial because eqs 6 and 7 contain the term a^{-3} to give the structure factors in dimension 1/volume. As pointed out above, $a = 8.12$ Å was chosen. In conjunction with N as the number of monomers, this accounts for the correct chain statistics. On the other hand, if a^3 (535 Å^3) is taken as the volume of a monomer, this value differs from the actual monomer volume (170 Å^3) by a factor of 3. So the value of a may be subject to dispute, and choosing a smaller value would raise the calculated Rayleigh ratios somewhat. We have used eq 10 (Θ-solvent conditions) to estimate the virial coefficient in the state of network preparation and measurement. Any other choice would lead to a significant drop of the calculated structure factors and thus widen the gap between theory and experiment.

These considerations show that by tuning the input parameters of the calculation some minor adjustment can be achieved, but the discrepancy between theory and experiment with regard to $R_{\text{gel}}(q)$ cannot be overcome. One possible reason was already mentioned at the outset: PR theory assumes that the gels are prepared in an athermal solvent and have a low degree of frozen heterogeneity, whereas the PNIPA hydrogels studied in this work were synthesized at conditions where the solvent quality is worse, possibly close to Θ conditions. Another potential explanation may be seen in the low cross-linking efficiencies (<10%) achieved in the experimental studies, which indicate the marked presence of nonidealities such as cyclizations or cross-link agglomerations. Since network formation took place by cross-linking copolymerization, a process passing through the microgel stage, strong heterogeneities are anticipated.

Conclusions

The influence of preparation conditions, such as preparation temperature, monomer concentration, and cross-linker concentration, on macroscopic properties and spatial inhomogeneities of PNIPA hydrogels was investigated by mechanical measurements and static light scattering. The cross-linking efficiency is almost independent of cross-linker concentration when the monomer concentration is fixed. While the modulus rises in proportion with cross-linker concentration, so does the excess Rayleigh ratio indicating that stronger cross-linking results in stronger inhomogeneity. When on the other hand the cross-linker concentration is kept constant, the shear modulus and the cross-linking efficiency increase with rising monomer concentration. Concurrently the Rayleigh ratio drops markedly, indicating that the higher the monomer concentration the more homogeneous are the gels thus formed. This is a consequence of the decreasing probability of cyclization and intramolecular cross-linking reactions. At fixed concentrations of both cross-linker and monomer, the cross-linking efficiency decreases markedly with rising preparation temperature of the gels. Since PNIPA exhibits a lower critical solution temperature around 32 °C, microgels formed in intermediate states of the cross-linking polymerization are less swollen when this temperature is approached, and thus, a greater extent of reaction is required to achieve a continuously interconnected gel. Less swollen microgels also mean that there is a larger concentration difference between microgels and surrounding solution. This heterogeneity is carried through to the final state of the gel and causes the strong increase of the observed Rayleigh ratio when the preparation temperature is raised from 20 °C to the LCST.

The results of light scattering measurements were compared to the predictions of PR theory not only qualitatively but also with regard to absolute intensities. This comparison reveals that the theoretical calculations show the same general tendency as the experimental findings. Moreover, the calculated thermal correlator, $R_{\text{sol}}(q)$, is close to the Rayleigh ratio actually measured for solutions of linear PNIPA. However, the calculated static correlator of the gels, $R_{\text{ex}}(q)$, is about 10 times smaller than found experimentally. In our view this discrepancy is a consequence of preparing the gels by cross-linking copolymerization and conducting the synthesis in a solvent worse than an athermal one. Both facts lead to much stronger inhomogeneities in the state of formation than presumed in PR theory. Therefore, it is to be expected that this theory does not apply quantitatively to the present case. The deviations observed go in the direction one would anticipate.

Acknowledgment. B.D. thanks Alexander von Humboldt Foundation for financial support. The authors thank J. Adams for help in static light scattering measurements.

References and Notes

(1) Dusek, K. In *Polymer Networks*; Stepto, R. F. T., Ed.; Blackie Academic & Professional: London, 1998; Chapter 3, pp 64−92.
(2) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1−62.
(3) Okay, O.; Nagash, H. J.; Capek, I. *Polymer* **1995**, *36*, 2413−2419.
(4) Dusek, K. In *Developments in polymerisation/3*; Haward, R. N., Ed.; Applied Science: London, 1982; p 143.
(5) Okay, O. *Polymer* **1994**, *35*, 796−807.
(6) Schröder, U. P.; Oppermann, W. *Macromol. Theory Simul.* **1997**, *6*, 151−160.
(7) Mallam, S.; Horkay, F.; Hecht, A. M.; Geissler, E. *Macromolecules* **1989**, *22*, 3356−3361.
(8) Horkay, F.; Hecht, A. M.; Geissler, E. *Macromolecules* **1994**, *27*, 1795−1798.
(9) Shibayama, M.; Norisuye, T.; Nomura, S. *Macromolecules* **1996**, *29*, 8746−8750.
(10) Shibayama, M.; Takata, S.; Norisuye, T. *Physica A* **1998**, *249*, 245−252.
(11) Takata, S.; Norisuye, T.; Shibayama, M. *Macromolecules* **1999**, *32*, 3989−3993.
(12) Nakamoto, C.; Motonaga, T.; Shibayama, M. *Macromolecules* **2001**, *34*, 911−917.
(13) Norisuye, T.; Masui, N.; Kida, Y.; Kida, Y.; Ikuta, D.; Kokufuta, E.; Ito, S.; Panyukov, S.; Shibayama, M. *Polymer* **2002**, *43*, 5289−5297.
(14) Norisuye, T.; Kida, Y.; Masui, N.; Tran-Cong-Miyata, Q.; Maekawa, Y.; Yoshida, M.; Shibayama, M. *Macromolecules* **2003**, *36*, 6202−6212.
(15) Takata, S.; Norisuye, T.; Shibayama, M. *Macromolecules* **2002**, *35*, 4779−4784.
(16) Lindemann, B.; Schröder, U. P.; Oppermann, W. *Macromolecules* **1997**, *30*, 4073−4077.
(17) Kizilay, M. Y.; Okay, O. *Macromolecules* **2003**, *36*, 6856−6862.
(18) Bastide, J.; Candau, S. J. In *The Physical Properties of Polymer Gels*; Cohen Addad, J. P., Ed.; John Wiley: New York, 1996; Chapter 5, pp 143−295.
(19) Shibayama, M. *Macromol. Chem. Phys.* **1998**, *199*, 1−30.
(20) Panyukov, S.; Rabin, Y. *Macromolecules* **1996**, *29*, 7960−7975.
(21) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(22) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clarendon Press: Oxford, U.K., 1975.
(23) László, K.; Kosik, K.; Rochas, C.; Geissler, E. *Macromolecules* **2003**, *36*, 7771−7776.
(24) Shild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163−249.
(25) Wu, C.; Zhou, S. *Macromolecules* **1995**, *28*, 8381−8387.
(26) Sayil, C.; Okay, O. *Polym. Bull.* **2000**, *45*, 175−182.
(27) Debye, P. J. *J. Chem. Phys.* **1959**, *31*, 680−687.
(28) Bueche, F. *J. Colloid Interface* **1970**, *33*, 61.
(29) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518−525.
(30) Soni, V. K.; Stein, R. S. *Macromolecules* **1990**, *23*, 5257−5265.
(31) Gao, J.; Wu, C. *Macromolecules* **1997**, *30*, 6873−6876.
(32) Kubota, K.; Fujishige, S.; Ando, I. *Polym. J.* **1990**, *22*, 15−20.
(33) Flory, P. J. In *Statistical Mechanics of Chain Molecules*; John Wiley & Sons: New York, 1969; Chapter 1, p 12.
(34) Shibayama, M.; Tanaka, T.; Han, C. C. *J. Chem. Phys.* **1992**, *97*, 6842−6854.
(35) Elias, H. G. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Abe, A., Bloch, D. R., Eds.; John Wiley & Sons: New York, 1999; Vol. VII, p 307.
(36) Higgins, J. S., Benoît, H. C. *Polymers and Neutron Scattering*; Clarendon Press: Oxford, U.K., 1994.

MA049169D