Influence of observation temperature on light scattering of poly-N-isopropylacrylamide hydrogels†

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Static and dynamic light scattering methods were applied to characterize the microstructure of gels synthesized by cross-linking copolymerization of N-isopropylacrylamide, with particular emphasis on the influence of measurement temperature. The total scattering intensity was divided into two parts: thermal scattering due to Brownian motion and static scattering due to topological or spatial inhomogeneity. Different methods of data evaluation, i.e. the non-ergodic and the partial heterodyne approaches, were carefully compared. We obtained consistent results clearly demonstrating that both parts of the scattering rise markedly upon increasing the observation temperature from 10 to 27.5 °C thus approaching the lower critical solution temperature. While the temperature dependence of the thermal scattering component is well understood, we attribute the rise of the static component to the establishment of local swelling equilibrium in a gel whose cross-link density features some inhomogeneity. This means that with rising temperature the more densely cross-linked regions deswell at the expense of the less densely cross-linked ones. As a result, the scattering contrast is enhanced thus leading to a larger static scattering intensity.

Introduction

Polymer gels are cross-linked systems composed of polymer and solvent. Since they have many practical applications such as in contact lenses, super absorbents, etc. many research groups concentrate on characterizing them and improving their properties. It is well established that polymer gels generally possess some kind of structure on length scales larger than the mesh size of the network. This is due to an uneven topological or spatial distribution of cross-links and, accordingly, polymer concentration, commonly referred to as spatial gel inhomogeneity, and can be caused by cyclization reactions, microgel formation during preparation, differences between the reactivities of functional groups, and diffusion controlled reactions.1,2 Although it is of considerable interest and attempts to attain detailed insight have been ongoing for decades, it is still not fully understood.

Light scattering and neutron scattering techniques are most frequently applied to investigate the structure and, in particular, the spatial inhomogeneities in gels. In the light scattering regime (low q-range, $q \ll 0.1 \text{ nm}^{-1}$), the scattering intensity from gels is generally markedly larger than that from a corresponding polymer solution, while the differences between gel and solution diminish significantly in the higher q-range ($q \gg 0.1 \text{ nm}^{-1}$) covered by small angle neutron scattering. The excess scattering is related to spatial inhomogeneity, and a number of theoretical approaches or models have been proposed for its interpretation.3–11 Another manifestation of the inhomogeneity is the appearance of a speckle pattern when a gel is illuminated with coherent light. In dynamic light scattering experiments, it is then observed that different locations within a gel scatter differently.12–16 Procedures to divide the total scattering intensity into two parts originating from thermal concentration fluctuations and from spatial network heterogeneity were developed in the early 90s.15,17

In this paper, we consider both static and dynamic light scattering methods to characterize the microstructure of gels synthesized by cross-linking copolymerization of N-isopropylacrylamide (NIPA).

Poly-N-isopropylacrylamide (PNIPA) in water forms a temperature sensitive polymer–solvent system with a lower critical solution temperature (LCST) around 34 °C. It is the prime example of a stimuli-responsive polymer, and an extensive literature exists covering studies of, e.g., its phase behavior,18–20 its potential in creating “intelligent” materials or devices,21–23 etc. Likewise, investigations on PNIPA gels by scattering methods are numerous. Shibayama et al. demonstrated that the spatial inhomogeneities increased with rising cross-link concentration and with rising preparation temperature of the gels.24 They also showed that the ensemble-average light scattering intensity increased when the gels were swollen, while the fluctuating part of the scattering intensity seemed to decrease upon swelling.25 The same group studied the effect of pressure at gel preparation,26,27 and they explored the influence of weak ionization of the...
polymer on the structure factor. Wu et al. studied the properties of PNIPA hybrid gels formed when a sufficiently concentrated dispersion of microgels was cooled from temperatures above the LCST to below the LCST. Their light scattering investigations showed that the static scattering component of the macroscopic gel attained by close-packing of the swollen microgel particles was due to large voids. These could be avoided when the temperature change occurred very slowly.  

Surprisingly, papers focusing on a detailed inspection of the dependence of scattering behavior on the observation temperature in the one phase region, below the LCST, are rather scarce. The main emphasis was focused on a study of the critical behavior and the collapse. Already in 1994, Tanaka et al. pointed out that the static spatial fluctuations reversibly increased with rising temperature and diverged at the spinodal line. This statement was applied to measurements close to the LCST (T > 25 °C), while data at lower temperatures were somewhat ambiguous. Later, Shibayama et al. confirmed the observation that the static and the fluctuating part of light scattering intensity, as well as the cooperative diffusion coefficient, are strongly dependent on the observation temperature. While this was expected for the latter two quantities, the authors concluded that there must be a strong coupling between static and fluctuating components. Koizumi et al. deduced from neutron scattering and spin echo data that, as the temperature was raised towards the LCST, the static scattering intensity increased more rapidly than the thermal component. They explained this behavior via the excluded volume parameter in the Panyukov Rabin theory, even though the theory was derived for gels made by instantaneous cross-linking of semidilute polymer solutions, which does not apply to the PNIPA gels studied.

The present study aims at a careful inspection of the influence of temperature on the static and thermal scattering components of PNIPA gels in the range 10–27.5 °C, i.e. below the LCST. Specifically, for a gel synthesized at 25 °C, light scattering measurements were performed at 25, 20, 15, 10, 12.5, 17.5, and 27.5 °C (in that sequence) in order to verify that the scattering properties are fully reversible with regard to a temperature variation within the range studied. Obviously, the thermal scattering should rise when the LCST is approached from lower temperatures. The dependence of the static scattering on temperature is not so clear and the few literature data diverge to some extent. In order to extract the excess part from dynamic light scattering experiments, we apply the non-ergodic and partial heterodyne approaches, thus separating the contributions of the dynamic or thermal concentration fluctuations and of the (static) inhomogeneities to the total scattering intensity. We also use the much simpler approach based on static scattering for comparison. We will show that both methods agree very well and that the static scattering varies with temperature to the same degree or slightly stronger than the thermal scattering.

**Consideration of light scattering and data evaluation**

In this paper, we will discuss the information obtained by light scattering methods on the microstructure of hydrogels. Two experimental methods have been applied, which, for simplicity, are referred to as static light scattering (SLS) and dynamic light scattering (DLS). In the current context, the use of these denotations may be somewhat misleading, because the dynamics is not our main concern. We just refer to DLS, when we employ an apparatus that is particularly devised and suited for DLS measurements, but we consider appropriate averages of scattering intensities. Analysis of the dynamics naturally yields the cooperative diffusion coefficient, but it is primarily required to be able to identify different fractions of the total scattering intensities. We will therefore review and compare the two methods with regard to what seems to be relevant for measurements on gels.

Scattering intensities obtained by SLS are usually reported in absolute units as Rayleigh ratios, \( R(q) \). Here, \( q = (4\pi n l_0 \sin (\theta/2)) \) is the amplitude of the scattering vector with \( \theta \) being the scattering angle, \( l_0 \) the wavelength of the incident light in a vacuum and \( n \) the refractive index of the medium, respectively. For gels, we then write

\[
R(q) = R_F(q) + R_C(q),
\]

where the total scattering intensity, \( R(q) \), has been split into two contributions: \( R_F(q) \), termed the dynamic or fluctuating part, is due to thermal concentration fluctuations and \( R_C(q) \), termed the static part, is due to spatial inhomogeneities possibly resulting from the cross-linking process. The latter is the quantity of interest to characterize the microstructure of the gels.

In a common SLS device, the detector has a wide aperture or slit, collecting the scattered light in a rather large solid angle (typically of the order of \( 10^{-3} \)). This results in a correspondingly small coherence area of order \( n^2/\Omega \), which is much smaller than the cross-section of the scattering volume. As a consequence, SLS measurements automatically report the scattering intensity as an ensemble average over the scattering volume. This comes usually pretty close to the macroscopic ensemble. Therefore, all quantities in eqn (1) represent ensemble averages.

In an experimental approach to determine \( R_C(q) \) from SLS measurements, one often presumes that the thermal fluctuations in a gel are practically identical with those in a solution of the linear polymer, hence \( R_F(q) \approx R_{SOL}(q) \), and \( R_C(q) \approx R(q) - R_{SOL}(q) \). \( R_{SOL}(q) \) becomes available by separately measuring the scattering intensity of a (semi-dilute or concentrated) solution of the uncross-linked polymer under conditions equivalent to those in the gel. Although this seems to be a plausible assumption, it is not generally valid. Geissler et al. showed by a series of carefully devised experiments based on a thorough theoretical treatment that \( R_F(q) \) is generally some 30% larger than \( R_{SOL}(q) \). In many cases, however, the static scattering intensity is so much larger than the thermal scattering that the appreciable error in \( R_F(q) \) becomes irrelevant or is plainly accepted. On the other hand, it is frequently difficult or even impossible to prepare a solution of the linear polymer. Either a polymer of exactly the same composition as that in the gel is not available, or the preparation of a homogeneous solution proves impractical because the viscosity is becoming too high.

In DLS, the detection optics is designed to achieve a large coherence factor. Modern instruments employ single-mode or few-mode light guides for this purpose. As a consequence, minor changes of the position or orientation of a gel sample produce marked variations of the measured scattering intensity, forming a so-called speckle pattern. While this behavior is typical...
of non-ergodic samples such as gels or disordered solids, it does not appear in fluids.

It is common in the literature on DLS to denote the scattering intensity by \( I(q) \). We stick to this custom, but we will report these intensities in absolute units to enable direct comparison with data measured by SLS. Hence, \( I(q) \) and \( R(q) \) are equal quantities, the different letters just refer to distinct measuring methods. Since it is the major purpose of DLS to measure intensities on the scale of \( \mu \)s and to analyze temporal intensity fluctuations, we explicitly indicate time averages by \((\ldots)_{T}\).

As stated above, the time-averaged scattering intensity \( \langle I(q)\rangle_{T} \) measured on a gel sample varies markedly with sample position or orientation. \( \langle I(q)\rangle_{T} \) has two contributions which can be written as\(^{34,37,35} \)

\[
\langle I(q)\rangle_{T} = \langle I_{v}(q)\rangle_{T} + I_{c}(q)
\]

Eqn (2) seems very similar to eqn (1), but there is a significant difference. Whereas eqn (1) applies to the sample as a whole because the intensities are ensemble averages, eqn (2) applies only to one particular speckle, i.e. a definite location in the sample observed under a definite scattering vector. \( \langle I_{v}(q)\rangle_{T} \) is the time average of the fluctuating component arising from dynamic, liquid-like concentration fluctuations. Because this contribution is ergodic, \( \langle I_{v}(q)\rangle_{T} \equiv R_{v}(q). \) On the other hand, \( I_{c}(q) \) is independent of time, but depends on position.\(^{44} \) That is why generally \( I_{c}(q) \neq R_{c}(q) \) and \( \langle I(q)\rangle_{T} \neq R(q). \) The remainder of this section is therefore concerned with determining the ensemble averages \( \langle I(q)\rangle_{E} \) or \( \langle I_{c}(q)\rangle_{E} \) respectively.

\( \langle I(q)\rangle_{E} \) can of course be obtained by taking measurements of scattering intensity on a sufficiently large number of positions and subsequent averaging, or by rotating the sample while the measurement is running. But these procedures alone do not allow for a separation of the different contributions. For that purpose, it is necessary to make use of the intensity correlation functions.

Basically, there are two approaches that have been described and discussed extensively in the literature. We therefore just quote the relevant equations used to analyze the experimental data.

According to Pusey and van Megen\(^{17} \) (non-ergodic method), \( \langle I_{v}(q)\rangle_{T} \) is related to \( \langle I(q)\rangle_{T} \) via

\[
\langle I_{v}(q)\rangle_{T} = \langle I_{v}(q)\rangle_{E} \left( 1 - f(q, \infty) \right)
\]

where \( f(q, \tau) \) is the normalized intermediate ensemble-averaged scattering function and \( f(q, \infty) \) its asymptotic value at \( \tau \rightarrow \infty \).

\( f(q, \tau) \) can in turn be calculated from the time-averaged intensity correlation function measured at a particular position, \( g^{(2)}_{T} \),

\[
f(q, \tau) = 1 + \frac{\langle I(q)\rangle_{T}}{\langle I(q)\rangle_{E}} \sqrt{\frac{g^{(2)}_{T}(q, \tau) - 1 - \sigma_{T}^{2}}{\beta} + 1 - 1}
\]

with

\[
g^{(2)}_{T}(q, \tau) = \frac{\langle I(q, 0)I(q, \tau)\rangle_{T}}{\langle I(q, 0)\rangle_{T}^{2}}
\]

and \( \sigma_{T} = g^{(2)}_{T}(q, 0) - 1 \), the initial amplitude of the time-averaged intensity correlation function, and the coherence factor of the instrument, \( \beta \).

The great attractiveness of this scheme is due to the fact that, in principle, the measurement of just one intensity correlation function at one particular position and the determination of the time-averaged scattering intensity at this position, \( \langle I(q)\rangle_{T} \), are sufficient to identify all desired quantities, provided we have measured \( \langle I(q)\rangle_{E} \) otherwise (cf. above). \( f(q, \tau) \) values calculated from different \( g^{(2)}_{T}(q, \tau) \) values characterizing different sample positions should be identical for a given system. The accuracy of this method, often termed the non-ergodic approach (NE), has also been assessed.\(^{46} \)

The alternative method, the partial heterodyne method (PH),\(^{19} \) is applicable if intensity correlation functions have been determined on a (large) number of positions. Then, apparent diffusion coefficients \( D_{A} \) can be estimated according to:

\[
D_{A} = -\frac{1}{2q^{2}} \lim_{\tau \rightarrow 0} \frac{d}{dt} \ln \left( g^{(2)}_{T}(q, \tau) - 1 \right)
\]

For different sample positions, different values of \( D_{A} \) are obtained, and these come along with different local scattering intensities \( \langle I(q)\rangle_{T} \). A relationship between \( D_{A} \) and the cooperative diffusion coefficient, \( D \), has been derived:

\[
D = (2 - \langle I_{v}(q)\rangle_{T}/\langle I(q)\rangle_{T})D_{A}
\]

Rearrangement of eqn (7) shows that a plot of \( \langle I(q)\rangle_{T}/D_{A} \) versus \( \langle I_{v}(q)\rangle_{T} \) should yield a straight line, from the slope and intercept of which the fluctuating component of the scattering intensity, \( \langle I_{v}(q)\rangle_{T} \), as well as \( D \) can be obtained. A sufficiently large number of data points are needed in order to define the straight line with adequate accuracy.

Both approaches described allow separation of the ensemble averaged scattering intensity into its components, \( \langle I_{v}(q)\rangle_{E} \) and \( \langle I_{c}(q)\rangle_{E} \). A separate measurement on a solution, as in the case of SLS, is not required.

**Experimental section**

**Synthesis of hydrogels and general characterization**

\( N \)-Isopropylacrylamide (NIPA, ACROS), \( N,N' \)-methylenebis(acrylamide) (MBA, Sigma), ammonium persulfate (APS, Sigma), and \( N,N',N' \)-tetramethylethylenediamine (TEMED, Sigma) were used as received. PNIPA gels were prepared by free-radical cross-linking copolymerization of NIPA and MBA in aqueous solutions. The initial monomer concentration \( C_{NIPA} \) was fixed at 704.2 mmol L\(^{-1} \) while the cross-linker concentration \( C_{MBA} \) was varied from 2.8 to 10.0 mmol L\(^{-1} \). A corresponding solution of the linear polymer was prepared under identical conditions without addition of MBA. The polymerization reactions were initiated using 3.5 mmol L\(^{-1} \) APS and 16.7 mmol L\(^{-1} \) TEMED. First, NIPA, MBA and TEMED were dissolved in distilled water and then the solution was purged with nitrogen gas for 10 min. After addition of the required amount of an APS solution, one part of the mixture was transferred between the plates of the rheometer maintained at the desired preparation temperature, \( T_{prep} \) (10, 15, 20, or 25 \( \pm 0.2 \) °C), and the remaining part was filtered through Teflon membrane filters (pore size: 0.45 \( \mu \)m) directly into NMR tubes serving as light scattering vials. Polymerization took place in these tubes being submerged in a water bath kept at the particular \( T_{prep} \). NMR tubes were
Rheological experiments

The shear moduli of the gels were measured with a parallel-plate rheometer (CVO Rheometer, Bohlin Instruments) equipped with a Peltier device for temperature control. The plates (diameter 40 mm) were set to a distance of 500 μm before the onset of the reactions. During all rheological measurements, a solvent trap was used to minimize solvent evaporation. A frequency of 1 Hz and a deformation amplitude of 2.0% was selected to ensure that the oscillatory deformation is within the linear regime. The polymerization process was monitored in situ by measuring the storage modulus $G'$ and loss modulus $G''$ as a function of time with the temperature being maintained at the desired $T_{\text{prep}}$. Both moduli reached final constant values after a few hours indicating completion of the polymerization. Then the temperature was changed in steps of 5 °C and the modulus was determined at temperatures different from $T_{\text{prep}}$ to obtain data at 15, 20, and 25 °C.

Results and discussion

1. Macroscopic characterization of the PNIPA gels

The hydrogels considered in this paper were all synthesized via free radical copolymerization of NIPA and MBA in an aqueous solution. The initial NIPA concentration $C_0$ was kept constant at 704.2 mmol L$^{-1}$ (80 g L$^{-1}$) while the cross-linker concentration was varied between 2.81 mmol L$^{-1}$ (0.4% of monomer) and 10.0 mmol L$^{-1}$ (~1.5% of monomer). Gels were prepared at $T_{\text{prep}} = 10, 15, 20,$ and 25 °C. In the subsequent discussion, we will focus on the gels made at 25 °C unless otherwise stated. The results obtained for gels made at the other preparation temperatures show essentially similar behavior; typical examples are given in the ESI.

For a macroscopic characterization, the shear modulus was measured and evaluated according to rubber elasticity theory yielding an estimate of the effective network density, $\nu_{\text{eff}}$, according to:47,48

$$G = \nu_{\text{eff}}(1 - 2f) \times R \times T \times \langle r^2 \rangle_0 / \langle r^2 \rangle$$  \hspace{1cm} (8)

Here $f$ is the functionality of the cross-links, hence for tetra-functional cross-links, $1 - 2f = 0.5$; $R$ is the gas constant, and $T$ the absolute temperature. $\langle r^2 \rangle$ is the mean-square end-to-end distance of network chains and $\langle r^2 \rangle_0$ the corresponding quantity for free chains. The calculation according to eqn (8) assumes that $G^*$, which is measured at 1 Hz, is identical to the equilibrium modulus within experimental error. This fact was substantiated by the finding that $G^*/G^* \approx 0.01$ in each case. However, $G^*$ showed an unusually strong temperature dependence, decreasing about 12% when the measurement temperature was lowered from 25 °C to 15 °C. Similar dependencies were found for gels made at 15 and 20 °C. The change with temperature was fully reversible. Possibly, this is due to a decrease of $\langle r^2 \rangle_0$ when the temperature approaches the LCST from below. Formation of associations represents another possibility that cannot be excluded. ($G^*$ rises even stronger above the LCST.) To estimate $\nu_{\text{eff}}$, we used $G(25^\circ \text{C})$ and assumed $\langle r^2 \rangle_0 / \langle r^2 \rangle = 1$ under preparation conditions.

Table 1 contains a list of the shear moduli of the gels prepared with different cross-linker concentrations and the quantities chosen because of their small wall thickness of ~0.6 mm, thus ensuring good heat transfer preventing a temperature rise due to the large negative enthalpy of polymerization.

The LCST was checked by visual inspection of several samples while slowly rising their temperature in a water bath. The solution became turbid at 33.0 °C (sharp transition), while for the gels a more gradual transition was observed with the onset of barely visible turbidity at 29–30 °C followed by a noticeable increase of turbidity at 33.5–34.5 °C. This behavior was confirmed by measuring the transparency in a spectrometer at 500 nm.

In supplemental experiments, weighed hydrogel samples were immersed in a large excess of water for 3 weeks to extract any soluble species. The water was replaced every second day. Eventually, the gels were dried in an oven at 55 °C. The water was replaced every second day. Eventually, the gels were dried in an oven at 55 °C. Weighed again. The gel fraction was determined as the final weight of the dry sample divided by the mass of monomer plus cross-linker in the initial gel sample. We found gel fractions of 90 ± 1%.

Light scattering measurements

SLS and DLS measurements were carried out at observation temperatures, $T_{\text{obs}}$, between 10 °C and 27.5 °C in steps of 2.5 °C. Specifically, for a gel synthesized at $T_{\text{prep}} = 25$ °C, light scattering measurements were performed at 25, 20, 15, 10, 12.5, 17.5, and 27.5 °C (in that sequence). Similar experiments were performed on gels synthesized at $T_{\text{prep}} = 20$ °C and 15 °C. Both apparatuses were employed with a He–Ne laser operating at $\lambda_0 = 633$ nm and were calibrated against a toluene standard for absolute intensity. SLS was performed on a goniometer SLS-2 (Fica). For measurements on gels, the cuvette was rotated about 60° between each cycle of data sampling to obtain the correct spatial averaging. For DLS, an ALV/CGS-3 compact goniometer (ALV, Langen, Germany) was used equipped with a cuvette rotation/translation unit (CRTU). A fiber optical detection unit based on three-mode detection was used, which includes an appropriate collimator/GRIN-lens fiber and the ALV/STATIC and DYNAMIC enhancer. Ideally, the three-mode detection unit gives an intercept in the time-averaged intensity autocorrelation function (ICF) $g_1(q,0) = 1$ of 0.33; i.e., $\beta$ should be 0.33. An experimental check with a polystyrene latex suspension gave a coherence factor $\beta$ of 0.36 ± 0.01, and this value was used for the evaluation of the DLS measurements. To protect the detector, the intensity of the incident light is automatically attenuated at each measurement by an eight-step automatic software-controlled attenuator and measured with a monitor diode. Thus, the intensity of incident light can be different within a series of measurements. When discussing scattering intensities, we therefore use data that were rescaled to a preset value of the monitor diode assuming a linear count rate dependence. Toluene was used as the index matching liquid. The temperature was controlled with an external thermostat. The time averaged ICFs were acquired at 100 different sample positions selected by randomly moving the CRTU before each run. The acquisition time for each run was 30 s. The ensemble-averaged scattering intensity, $\langle I(q) \rangle_E$, was determined by continuously moving the sample vial with the CRTU, and the acquisition time for $\langle I(q) \rangle_E$ was 2 min.
derived thereof. In addition to the effective network density, we have calculated the average molar mass of the network chains, \( M_C \), according to \( M_C = C_0 r_{\text{eff}} \), where \( C_0 \) is the mass concentration. The large values obtained for \( M_C \) indicate that an effective network chain is likely to consist of branched and cycled structures.

It is useful to compare the effective network density, \( r_{\text{eff}} \), with the hypothetical network density, \( r_{\text{ph}} \), of a network where all cross-links are perfectly interconnected by elastically effective network chains. This latter quantity was calculated from the molar concentration of the cross-linker in the system, \( C_{\text{MBA}} \), by assuming that all cross-linker molecules have completely reacted as tetrafunctional junction points: \( r_{\text{ph}} = 2C_{\text{MBA}} \). 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 ratio \( r_{\text{eff}}/r_{\text{ph}} \) (cross-linking efficiency) can serve as a measure for the extent of perfection. It is included in Table 1 as well. The values obtained are almost independent of the cross-linker concentration. They are considerably smaller than 1 indicating a preponderance of network imperfections.

2. Microstructure

An aqueous system containing linear PNIPA has a lower critical solution temperature (LCST) around 34 °C (we found 33.0 °C for our system). Below the LCST, it forms a homogeneous solution. However, concentration fluctuations increase when the temperature gets closer to the miscibility gap. Stated otherwise, water is a good solvent for PNIPA at low temperature, but the solvent quality drops significantly with rising temperature. This thermodynamic behavior gives rise to an increase of scattering intensities on the microstructure of PNIPA hydrogels, static light scattering experiments were carried out in the range 10 °C ≤ \( T_{\text{obs}} \) ≤ 27.5 °C on these gels as well as on the corresponding solution. The scattered light intensities, \( R(q) \), were recorded at scattering angles from 50° to 140°, which corresponds to a scattering vector range of \( q = 1.1 \times 10^2 \) to \( 2.5 \times 10^3 \) cm\(^{-1}\).

Fig. 1 shows the total scattering intensity \( R(q) = R_C(q) + R_{\text{Sol}}(q) \) vs. the square of the scattering vector \( q^2 \) for the hydrogels prepared at 25 °C with various amounts of MBA at different observation temperatures. Increasing the MBA concentration and observation temperature increases \( R(q) \) of the hydrogels. The change with temperature is fully reversible. It should be mentioned that \( R_{\text{Sol}}(q) \) rises from \( 1.02 \times 10^{-4} \) cm\(^{-1}\) at 15 °C to \( 1.82 \times 10^{-4} \) cm\(^{-1}\) at 25 °C. These results obviously show that the static portion of the scattered light from the PNIPA hydrogels is strongly temperature dependent. The angular dependence is too small to be exploited.

2.1 SLS. As mentioned further above, SLS measurements automatically report the scattering intensity as an ensemble average over the scattering volume, being close to a macroscopic ensemble. This was verified by repetition of the measurements after turning or shifting the sample and checking for reproducibility. Usually an average over 5 different positions was taken.

To investigate the influence of observation temperature on the microstructure of PNIPA hydrogels, static light scattering experiments were carried out in the range 10 °C ≤ \( T_{\text{obs}} \) ≤ 27.5 °C on these gels as well as on the corresponding solution. The scattered light intensities, \( R(q) \), were recorded at scattering angles from 50° to 140°, which corresponds to a scattering vector range of \( q = 1.1 \times 10^2 \) to \( 2.5 \times 10^3 \) cm\(^{-1}\).

Table 1 Results of rheological measurements obtained on gels made with different cross-linker concentrations. Monomer concentration \( C_{\text{NIPA}} = 704.2 \) mM corresponding to 7.15 vol%.

<table>
<thead>
<tr>
<th>( C_{\text{MBA}} ) mmol L(^{-1} )</th>
<th>( G'(25 ) °C)/kPa</th>
<th>( r_{\text{eff}} )/mol m(^{-3} )</th>
<th>( M_C )/g mol(^{-1} )</th>
<th>( r_{\text{eff}}/r_{\text{ph}} )</th>
</tr>
</thead>
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<tr>
<td>2.81</td>
<td>0.93</td>
<td>0.75</td>
<td>100 000</td>
<td>0.132</td>
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<td>4.69</td>
<td>1.80</td>
<td>1.44</td>
<td>55 000</td>
<td>0.154</td>
</tr>
<tr>
<td>7.04</td>
<td>2.37</td>
<td>1.91</td>
<td>42 000</td>
<td>0.135</td>
</tr>
<tr>
<td>8.80</td>
<td>2.94</td>
<td>2.36</td>
<td>34 000</td>
<td>0.134</td>
</tr>
<tr>
<td>10.0</td>
<td>3.25</td>
<td>2.60</td>
<td>31 000</td>
<td>0.131</td>
</tr>
</tbody>
</table>

![Fig. 1] Total scattering intensity \( R(q) \) plotted versus \( q^2 \) for PNIPA hydrogels at different measurement temperatures, \( T_{\text{obs}} \) and MBA concentrations, \( X \), as indicated. \( T_{\text{prep}} = 25 \) °C.
Variation of time averaged scattering intensity \( I_{T} \) with sample position for PNIPA hydrogels with (a) 0, (b) 4.69, (c) 8.80, and (d) 10.0 mM MBA concentration. The solid lines represent the ensemble-averaged scattered intensity, \( \langle I_{E} \rangle \). The fluctuating components of the scattering intensity, \( \langle I_{E} \rangle_{T} \), are represented by the dashed and dotted lines. \( T_{\text{obs}} = T_{\text{prep}} = 25 \, ^{\circ}\text{C}; \theta = 90^\circ. \)

The solid horizontal lines represent the ensemble average of scattering intensity, \( \langle I_{E} \rangle \), obtained, on the one hand, by calculating the mean value of the data obtained at 100 positions, and, on the other hand, the value measured while the cuvette was steadily rotated. There is a slight difference between the two values reflecting experimental uncertainty. The dashed line indicates the fluctuating component of the scattered intensity, \( \langle I_{E} \rangle_{T} \), estimated by the partial heterodyne method (based on 100 positions, eqn (7)), while the dotted line gives the result for \( \langle I_{E} \rangle_{T} \) when the non-ergodic method was applied on just 15 positions (eqn (3)), with subsequent averaging. The essential features deduced from Fig. 2 are as follows: there is no appreciable discrepancy between the two methods of data evaluation (we will elaborate on this point further below). While \( \langle I_{E} \rangle \) increases significantly with rising cross-link density, the fluctuating component, \( \langle I_{E} \rangle_{T} \), remains practically constant and is identical to the scattering intensity of a solution 1.8 \times 10^{-4} \, \text{cm}^{-1}.

To analyze the influence of observation temperature on the scattering behavior, we focus on the sample having 8.8 mmol L^{-1} MBA, shown in Fig. 2c. Fig. 3 shows the corresponding data measured at 10, 15, 20, and 25 \, ^{\circ}\text{C} at \( \theta = 90^\circ. \) It is obvious that the spatial fluctuations of \( \langle I_{E} \rangle_{T} \) grow significantly with rising temperature, and so do the ensemble averages. The change with temperature is fully reversible. Closer inspection shows that the fluctuating component, \( \langle I_{E} \rangle_{T} \), is also rising with temperature. This is easier seen in a compilation of the data given in Table 2. Columns 2 and 3 represent \( \langle I_{E} \rangle_{T} \) determined by the partial heterodyne method and the non-ergodic method, respectively. Columns 4 and 5 show, for comparison, the scattering intensity of a PNIPA solution measured in the two apparatus. All 4 values agree to within \( \pm 20\% \) at each temperature, while there is a distinct increase with rising temperature. This increase is expected, of course, because the thermal fluctuations become stronger when the LCST is approached.

The last three columns in Table 2 show the constant component of scattering intensity, \( I_{C} \), obtained via the partial heterodyne method and the non-ergodic method, respectively, as well as \( R_{C} \), obtained by SLS (eqn (1)). Again, the data agree satisfactorily at each temperature. However, there is a marked increase with rising temperature, seemingly even stronger than that of \( \langle I_{E} \rangle_{T}. \) This observation requires further discussion.

If one erroneously assumed that the static scattering was due to some permanently fixed, solid-like heterogeneity, there would be no influence of temperature on \( I_{C}. \) Obviously, this is not correct. In fact, the increase of \( I_{C}(q) \) with rising temperature for PNIPA gels below the LCST was already reported by Tanaka et al.\textsuperscript{13} and Shibayama et al.\textsuperscript{14,15} but without giving an in-depth explanation. They showed that above the LCST (36–50 \, ^{\circ}\text{C}) for weakly charged PNIPA gels, \( I_{C} \) rises markedly with increasing observation temperature due to the progressive formation of a two-phase structure, while \( \langle I_{E} \rangle_{T} \) remains essentially constant.\textsuperscript{29}

Considering the scattering behavior in the homogeneous region below the LCST, we proceed from the notion that a given polymer network generally has an inhomogeneous distribution of cross-links. Hence, the local cross-link density (in an area defined by the static correlation length) is fixed through synthesis. This local cross-link density controls the local polymer concentration depending on thermodynamic conditions. It is predominantly the polymer density correlation function that determines the scattering properties of the gel, not the refraction index increment of the cross-linking moieties is by far greater than that of the polymer. The temperature dependence of the static scattering intensity \( I_{C}(q) \) therefore arises from the thermodynamics of variable local swelling.

The swelling pressure of a gel is given by the osmotic pressure of a semi-dilute solution of the uncross-linked polymer plus the negative pressure due to chain elasticity.\textsuperscript{49} The osmotic pressure, as a crude approximation, changes in proportion with excluded volume, or \( (1 - 2\chi) \), where \( \chi \) is the Flory interaction parameter. For PNIPA, \( \chi \) varies strongly with temperature and approaches 0.5 near the LCST. On the other hand, the pressure due to chain elasticity is nearly independent of solvent quality, but proportional to cross-link density. Now consider regions of high cross-link density in equilibrium with regions of lower cross-link density. At a given temperature, say 20 \, ^{\circ}\text{C}, this equilibrium results in distinct variations of local polymer concentration. As the temperature is raised, the osmotic part of the swelling pressure becomes smaller while the elastic part becomes more dominant. This means that the more densely cross-linked regions deswell at the expense of the less densely cross-linked ones. (The overall volume is kept constant, of course; the gel is not in macroscopic equilibrium with pure solvent.) As a result, the characteristic length scales of the structure do not change, but the scattering contrast is enhanced, resulting in larger static scattering intensity.
By this argument, the temperature dependence of $I_C(q)$ is traced back to the same origin as that of $\langle I_F(q) \rangle_T$, namely solvent quality. This does not necessarily mean, however, that the form of the dependence is similar. Thermal fluctuations, giving rise to $\langle I_F(q) \rangle_T$, are governed by the course of the spinodal, while the static concentration contrast, giving rise to $I_C(q)$, results from local swelling equilibrium.

In order to compare the temperature dependencies of the two components, it is worthwhile to look at the normalized intermediate scattering functions calculated from the measured $g_1^q(t)$ by eqn (4). Fig. 4 shows the averaged $f(q,\tau)$ functions for $q = 1.9 \times 10^8$ cm$^{-1}$ corresponding to a scattering angle of $90^\circ$. At long times they reach asymptotic plateau values that increase slightly with rising measuring temperature and that are indicative of the frozen-in inhomogeneity. According to the theory derived by Pusey and van Megen, the $f(q,\tau)$ curves measured at one temperature on a given gel should be identical irrespective of the sample position. Actually, there is quite some scatter in these plateau values. Table 3 therefore shows a list of the average values together with their standard deviations derived from measurements at 15 positions. They were obtained by fitting of the data to the expression

$$f(q,\tau) = f(q,\infty) + A \exp \left(-\frac{\tau}{\tau}\right)$$

using a nonlinear least-squares fitting procedure.

$f(q,\infty)$, i.e. the (ensemble averaged) fraction of scattered light which is due to static inhomogeneities, increases moderately from around 70% to around 80% when the measuring temperature is raised from 10 °C to 25 °C. This rise is clearly beyond experimental uncertainty and proves that the static scattering component is affected by temperature to a greater extent than the fluctuating component.

The correlation time, $\tau$, is around 70 $\mu$s corresponding to cooperative diffusion coefficients, $D$, between 35 and 43 $\mu$m$^2$s$^{-1}$. $D$ rises moderately with increasing cross-link density, while the influence of temperature is amazingly small (less than 5% change when the observation temperature was increased from 10 to 25 °C, i.e. within the experimental error). Since the viscosity of water drops by 30% in that range, there is likely an opposing effect based on some structural rearrangement. The correlation lengths in the range 5–7 nm compare well with the mean distance between cross-links.

Fig. 5 shows a side-by-side comparison of the temperature dependences of scattering intensity measured by SLS and DLS for a range of cross-link densities for gels prepared at 25 °C. (Gels prepared at 20 °C and 15 °C give similar results as shown in Fig. S1 and S2 in the ESI†.) Note that $\langle I_F \rangle_T$ corresponds to $R_R$ and $\langle I_F \rangle_L$ corresponds to $R(q)$. The two graphs are closely identical. This is of course taken for granted as far as the ensemble-averaged total scattering intensities are concerned. In this case, the two methods just differ in the fact that the SLS apparatus yields the ensemble average directly, while with the DLS apparatus, the averaging must be performed deliberately either by rotating the cuvette during the measurement or by taking the average over a sufficiently large number of measurements taken at different sample positions. The procedures applied to obtain the fluctuating components, however, are fundamentally different. In SLS, the polymerization was carried out without a cross-linker, and the scattering intensity of the resulting solution is assumed to represent the fluctuating component of correspondingly synthesized gels. In DLS, the intensity correlation functions obtained on the gels were used to extract the fluctuating part. This could be done for each degree of cross-linking. Fig. 5 shows that the $\langle I_F \rangle_T$ data form one single line (open symbols in Fig. 5a), and that this line is pretty much the same as that of the solution (open symbols in Fig. 5b). These observations strongly support the notion that the two experimental approaches are equivalent. Fig. 5 further demonstrates that the discussion about the slightly different temperature

<table>
<thead>
<tr>
<th>$T_{obs}$</th>
<th>$I_F$ (PH)</th>
<th>$I_F$ (NE)</th>
<th>$I_{F,SOL}$ (DLS)</th>
<th>$R_{F,SOL}$ (SLS)</th>
<th>$I_C$ (PH)</th>
<th>$I_C$ (NE)</th>
<th>$R_C$ (SLS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 °C</td>
<td>1.23</td>
<td>1.03</td>
<td>1.04</td>
<td>0.76</td>
<td>1.95</td>
<td>2.17</td>
<td>1.92</td>
</tr>
<tr>
<td>15 °C</td>
<td>1.31</td>
<td>1.14</td>
<td>1.27</td>
<td>1.02</td>
<td>2.82</td>
<td>2.93</td>
<td>2.70</td>
</tr>
<tr>
<td>20 °C</td>
<td>1.74</td>
<td>1.46</td>
<td>1.71</td>
<td>1.50</td>
<td>3.73</td>
<td>4.36</td>
<td>4.24</td>
</tr>
<tr>
<td>25 °C</td>
<td>2.37</td>
<td>1.92</td>
<td>1.87</td>
<td>1.82</td>
<td>6.99</td>
<td>8.65</td>
<td>7.17</td>
</tr>
</tbody>
</table>

Table 2 Intensity values (in $10^{-5}$ cm$^{-1}$) of the fluctuating ($I_F$) and frozen ($I_C$) part in dynamic and static light scattering at different observation temperatures. $\theta = 90^\circ$, $C_{MBA} = 8.80$ mM, $T_{prep} = 25$ °C

![Fig. 4 Normalized intermediate ensemble-averaged scattering functions, $f(t)$, calculated from $g_1^q(t)$ values according to eqn (4) for different observation temperatures, $T_{prep} = 25$ °C.](image)

Table 3 List of the average values of $f(q,\infty)$ together with their standard deviations derived from measurements at 15 positions

<table>
<thead>
<tr>
<th>$T_{obs}$</th>
<th>$f(q,\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 °C</td>
<td>0.68 ± 0.057</td>
</tr>
<tr>
<td>15 °C</td>
<td>0.71 ± 0.047</td>
</tr>
<tr>
<td>20 °C</td>
<td>0.74 ± 0.035</td>
</tr>
<tr>
<td>25 °C</td>
<td>0.80 ± 0.036</td>
</tr>
</tbody>
</table>
possible scattering component in order to obtain some information on the slope of the intensity $I_\text{sc}$.

The major emphasis of the present work was on a detailed comparative investigation of the scattering patterns obtained by different methods of dividing the total scattering intensity into two parts: the thermal scattering component rises strongly with increasing the cross-link density. The major emphasis of the present work was on a detailed inspection of the dependence on the observation temperature of the thermal and static scattering components of a given gel. Earlier publications showed that both parts seem to increase when the temperature was raised, but this became evident only in a rather narrow temperature window, from 30–33 °C, close to the LCST. Our present results clearly show that both components also increase perceptibly in the range 10 °C ≤ $T_{\text{obs}}$ ≤ 25 °C, much further away from the LCST of PNIPA in water. The increase of the thermal scattering is expected, of course, because thermal fluctuations become stronger when the LCST is approached. However, the static component of scattering intensity is affected by temperature to an even greater extent. We interpret this behavior by assuming local swelling equilibrium in a gel whose cross-link density features some inhomogeneity. Equilibrium swelling is controlled by two competing factors, osmotic pressure and chain elasticity. The osmotic pressure of a semi-dilute polymer solution given by the Flory–Huggins equation scales, to a first approximation, with excluded volume, or $(1 - 2\chi)$, where $\chi$ is the Flory interaction parameter. For PNIPA, $\chi$ rises with temperature and approaches 0.5 near the LCST. Hence, the osmotic pressure decreases with rising temperature, while the chain elasticity remains essentially constant. This means that upon raising the temperature, more densely cross-linked regions deswell at the expense of the less densely cross-linked ones. Accordingly, the scattering contrast is enhanced thus leading to a larger static scattering intensity, as first pointed out by Tanaka et al.13

By following this argument we suppose that both parts of the scattering intensity are governed by thermodynamic quantities, namely quality of the solvent. However, different dependencies apply thus leading to the fact that the static scattering seems to be slightly more sensitive to temperature than the thermal scattering intensity. Our interpretation based on local swelling equilibrium is in accord with the view that polymer gels possess restricted ergodicity.10 They have an inhomogeneous distribution of cross-links, but their density-inhomogeneity is not fixed. Rather it is dependent on the establishment of local swelling equilibrium controlled by a distinct network topology.

**Conclusions**

Static and dynamic light scattering measurements were performed on PNIPA hydrogels in order to carefully compare different methods of dividing the total scattering intensity into two parts: thermal scattering due to Brownian motion of the network chains and static scattering due to topological or spatial inhomogeneity. All methods investigated yield consistent results and, in the first place, confirm the well-known fact that the static component rises strongly with increasing the cross-link density. The major emphasis of the present work was on a detailed inspection of the dependence on the observation temperature of the thermal and static scattering components of a given gel. Earlier publications showed that both parts seem to increase when the temperature was raised, but this became evident only in a rather narrow temperature window, from 30–33 °C, close to the LCST. Our present results clearly show that both components also increase perceptibly in the range 10 °C ≤ $T_{\text{obs}}$ ≤ 25 °C, much further away from the LCST of PNIPA in water. The increase of the thermal scattering is expected, of course, because thermal fluctuations become stronger when the LCST is approached. However, the static component of scattering intensity is affected by temperature to an even greater extent. We interpret this behavior by assuming local swelling equilibrium in a gel whose cross-link density features some inhomogeneity. Equilibrium swelling is controlled by two competing factors, osmotic pressure and chain elasticity. The osmotic pressure of a semi-dilute polymer solution given by the Flory–Huggins equation scales, to a first approximation, with excluded volume, or $(1 - 2\chi)$, where $\chi$ is the Flory interaction parameter. For PNIPA, $\chi$ rises with temperature and approaches 0.5 near the LCST. Hence, the osmotic pressure decreases with rising temperature, while the chain elasticity remains essentially constant. This means that upon raising the temperature, more densely cross-linked regions deswell at the expense of the less densely cross-linked ones. Accordingly, the scattering contrast is enhanced thus leading to a larger static scattering intensity, as first pointed out by Tanaka et al.13

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**References**

45 Macromolecules 2004, 37, 2944–2953, Norisuye et al. reported that $\langle I_3(q) \rangle_T$ is also dependent on the position. However, this variation is extremely small compared to that of $I_4(q)$ and will not be considered here.