

# Effect of crosslink density and amount of charges on poly(acrylamide-*co*-2-acrylamido-2-methyl-1-propanesulphonic acid) gel structure

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## Abstract

The network inhomogeneities and dynamics of polyelectrolyte copolymer gels formed by crosslinking poly(acrylamido-*co*-2-acrylamido-2-methyl-1-propanesulphonic acid) (poly(AAm-*co*-AMPS)) gels with *N,N'*-methylene-bis-acrylamide (MBAAm) were studied using the light scattering (LS) technique. Combining static and dynamic light scattering data, static-structure network inhomogeneities and dynamic concentration fluctuations were separated and their proportions in the total light scattering intensity were estimated. The effects of the network crosslink density and the amount of charged comonomer in poly(AAm-*co*-AMPS) gel were investigated. Strong, but opposite effects of those parameters on the presence of static-structure inhomogeneities were revealed. The dynamics of poly(AAm-*co*-AMPS) gel was found to be greatly affected by variations in the AMPS content of the gels. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Poly(acrylamido-*co*-2-acrylamido-2-methyl-1-propanesulphonic acid) (poly(AAm-*co*-AMPS)); Light scattering technique; Polyelectrolyte copolymer gels

## 1. Introduction

It is well known that the physical properties of a material are directly related to its structure. For the case of polymeric gels, properties such as swelling behavior (e.g. kinetics of swelling, volume phase transition), mechanical properties (e.g. elasticity), optical properties and permeability, are dependent on the gel network structure, which in turn depends on the conditions at gel preparation and conditions at measurement.

Non-ergodicity and structural inhomogeneities are usual features of the gel network [1,2], and are consequences of the nature of the process of network formation. If it is assumed that the network is formed instantaneously, or in a short period of time, the dynamics of concentration fluctuations of the pre-gel solution of monomers can be considered as topologically ‘frozen’ in the final network structure [3]. In addition, owing to the crosslinking process the polymer chain distribution in the network tends to increase the local polymer concentration in the vicinity of

junctions, compared with the mean polymer concentration in the gel. The implication is that the network structure contains quasi-static structural inhomogeneities, whose position is ‘independent’ of time, in addition to time-dependent inhomogeneities due to dynamic, thermal concentration fluctuations [4–7].

The network inhomogeneities have been widely studied for various neutral polymer gels [4,8]. In the case of polyelectrolyte polymer gels, where ionizable groups are present on polymer chains, repulsion between like charges leads to additional alteration of the network structure [9,10]. In most studies on polyelectrolyte gels, the fraction of charges has been controlled by changing the dissociation equilibrium of the ionizable component, by controlling the pH.

In recent years it has been shown [4,8,11,12] that scattering techniques, such as light scattering (LS), small-angle neutron scattering (SANS), and small-angle X-ray diffraction (SAXS) are useful tools in investigation of polymer gel network structure. The excess of scattering intensity from polymer gels, with respect to semi-dilute solutions of the same polymer at the same concentrations, has been found to depend on the preparation method [5], the crosslink density [7], the swelling ratio [5], and the degree of ionization [11].

Combining results from static scattering methods and techniques which sense the dynamic fluctuations of the

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gel network, e.g. dynamic light scattering (DLS), it becomes possible to distinguish the contributions from static-structure inhomogeneities and dynamic concentration fluctuations in the gel network.

The theoretical framework for scattering from non-ergodic media developed by Pusey and van Megen [13], has been successfully applied to study of polymer gel systems. Several methods of analyzing DLS data have been developed [13–15], and have been reviewed and compared by Fang and Brown [16]. The collective diffusion coefficient, obtained from the decay rate of the DLS auto-correlation spectrum [17–19], provides information about gel dynamics.

The objective of this study is to investigate the microstructure and dynamics of poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulphonic acid) gel, poly (AAM-co-AMPS). The sulphonic acid group on AMPS can dissociate extensively in a wide pH range, so that adjustment of pH is not necessary [20]. The amount of charges in the polymer gel can be approximated by the amount of AMPS comonomer. We report the effect of changing the crosslink density and the comonomer composition on the presence of spatial structural inhomogeneities and dynamic concentration fluctuations in the poly(AAM-co-AMPS) gel system.

## 2. Theoretical background

The extent of spatial inhomogeneities in polyelectrolyte gels is determined by a large number of parameters [21]. In addition to the chemical structure of the monomers, the distance from the phase boundary at gel preparation (i.e. temperature), polymer concentration at preparation, amount of crosslink molecules present in the pre-gel solution and degree of ionization may have an effect. Furthermore, a number of parameters at observation, such as extent of swelling, quality of solvent, temperature at observation and the presence of salt are relevant.

From scattering experiments (LS, SANS) it is clear that concentration fluctuations of gels comprise both static inhomogeneities (frozen structure) and dynamic fluctuations [6,22]. The scattering intensity can be written as follows [6]:

$$I(q) \cong \langle I(q) \rangle_T = I_{C,p}(q) + \langle I_F(q) \rangle_T \quad (1)$$

where  $I(q)$  is the total scattering intensity.  $I_C(q)$  and  $I_F(q)$  are the scattering intensities due to the static-structure inhomogeneities and dynamic concentration fluctuations, respectively.  $\langle \dots \rangle_T$  denotes time average.

Strong variations of the time-averaged scattering intensity with the position of the scattering volume have been found experimentally in the case of different kinds of gels [3,7,11,18]. The position dependent quantity is  $I_C(q)$ ,

and hence the ensemble average is:

$$\begin{aligned} \langle I(q) \rangle_E &= \lim_{P \rightarrow \infty} \frac{1}{P} \sum_{p=1}^P [I_{C,p}(q) + I_F(q)] \\ &= \langle I_C(q, t) \rangle_E + \langle I_F(q, t) \rangle_E \end{aligned} \quad (2)$$

Consequently, for non-ergodic media such as polymer gels, the time-averaged correlation function of the intensity of scattered light is different from the ensemble-averaged function. In a DLS experiment on polymer gel the intensity time correlation function at a particular sample position is given by the equation [6,13,23]:

$$C(q, \tau) = 1 + \alpha \sigma_1^2 \exp[-2D_{app} q^2 \tau] + \varepsilon \quad (3)$$

where  $\sigma_1^2$  denotes the initial amplitude of  $C(q, \tau)$ ,  $D_{app}$  is the apparent diffusion coefficient obtained at a given sample position and varies with the sample position in the range:  $D(\text{pure heterodyne mode}) \leq 2D_{app} \leq 2D(\text{pure homodyne mode})$ ,  $\varepsilon$  ( $\approx 0$ ) is the time-independent background. From the exponential decay of function (3)  $D_{app}$  can be obtained.

In the case of polymer gels the diffusion coefficient that characterizes the whole gel sample is called a collective (or cooperative) diffusion coefficient [19,24],  $D_c$ . The collective diffusion coefficient is proportional to the osmotic longitudinal modulus,  $M_{os}$  [25,26], and therefore also to the osmotic bulk modulus,  $K_{os}$ , and shear modulus,  $G$ :

$$D_c = M_{os}/f = (K_{os} + 4G/3)/f \quad (4)$$

where  $f$  is the friction coefficient between the polymer network and the solvent.

The osmotic bulk modulus,  $K_{os}$ , is related to the isotropic swelling pressure,  $\pi$ , exerted by the gel swelling in excess solvent:

$$K_{os} = \phi(\partial \pi / \partial \phi) \quad (5)$$

where  $\phi$  is the polymer volume fraction.

The partial heterodyne method according to Joosten and co-workers [14,18] gives the collective diffusion coefficient of non-ergodic medium,  $D_c$ , determined by plotting  $D_{app}$  as a function of time-averaged light scattering intensity  $\langle I(q) \rangle_T$  [23]:

$$\frac{\langle I(q) \rangle_T}{D_{app}} = \frac{2}{D_c} \langle I(q) \rangle_T - \frac{\langle I_F(q) \rangle_T}{D_c} \quad (6)$$

From the slope and intercept of Eq. (6),  $D_c$  and the fluctuating component of the time-averaged light scattering intensity,  $\langle I_F(q) \rangle$ , (and hence the scattering intensity due to the static-structure inhomogeneities,  $I_C(q)$ .) can be obtained.

## 3. Experimental

### 3.1. Sample preparation

Gels were prepared by free radical copolymerization of

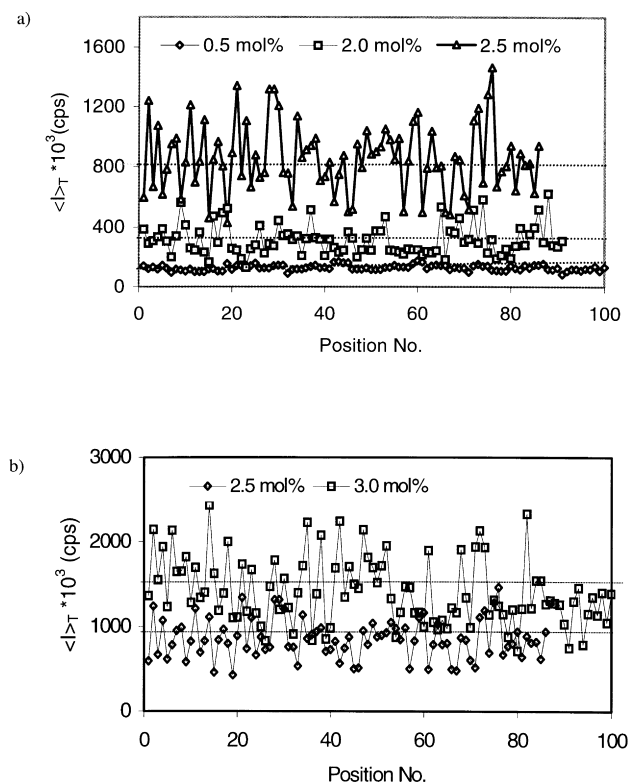


Fig. 1. Position dependence of the time-averaged light scattering intensity  $\langle I \rangle_T$  for poly(AAm-co-AMPS) gels with 0.8 mol% of AMPS and MBAAM as indicated on the graphs. Dotted lines represent the ensemble averages.

recrystallized acrylamide (Serva), acrylamido-2-methyl-1-propanesulphonic acid (Merck) and *N,N'*-methylene-bis-acrylamide (MBAAM) (Serva) as a crosslinking agent, dissolved in milli-Q water.

The total monomer concentration,  $c_T$ , was kept constant at  $850 \text{ mmol dm}^{-3}$ , and the amounts of MBAAM and AMPS were varied in the range from 0 (solution) to 3.5 mol%, and 0 (non-ionic) to 4.0 mol%, respectively. When MBAAM was varied the amount of AMPS was 0.8 mol%, and when AMPS was varied the MBAAM content was kept at 3.0 mol%. The pre-gel solution was filtered through a  $0.2 \mu\text{m}$  filter into glass ampoules with internal diameter approximately 10 mm. The solutions were purged with  $\text{N}_2$  for a few minutes, and the gelation reaction, initiated by

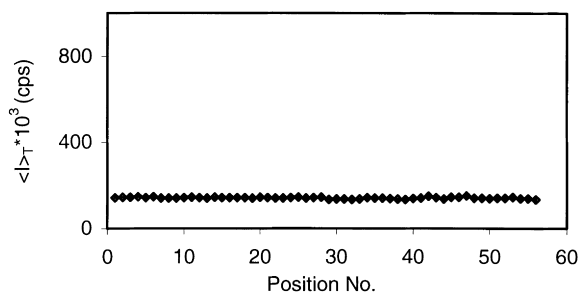


Fig. 2. The time-averaged light scattering intensity  $\langle I \rangle_T$  for the solution of poly(AAm-co-AMPS) with 0.8 mol% of AMPS.

ammonium persulfate ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) was carried out at  $70^\circ\text{C}$  for 1 h. The gels were left at room temperature, and used for DLS experiments the following day, thus allowing the reaction to be completed.

### 3.2. Light scattering experiments

In order to obtain an ensemble average of time-averaged light scattering intensities, static and dynamic light scattering data acquisitions were performed by rotating the sample 50–100 times. The total time-averaged scattering intensity,  $\langle I(q) \rangle_T$ , and intensity correlation curve,  $C(q, \tau)$ , were collected for each position.

Static light scattering experiments were performed using a DAWN light scattering instrument, with an Ar laser operating at 488 nm. The experimental temperature was  $30.0 \pm 0.2^\circ\text{C}$ . The gel samples were allowed to reach thermal equilibrium prior to the beginning of the experiments. The total time-averaged scattering intensity,  $\langle I(q) \rangle_T$ , was recorded for an angle of  $79.5^\circ$ , which corresponds to the scattering vector of magnitude  $q = (4\pi n/\lambda) \sin(\theta/2) = 1.65 \times 10^{-3} \text{ \AA}^{-1}$ .

A photon correlator (Nicomp Model 370 (Pacific Scientific) Submicron Particle Sizer, with 64 linear channels), was used in the DLS experiments to collect correlation functions,  $C(q, \tau)$ . Sampling times, i.e. channel widths were chosen automatically according to the relaxation rate of the gels, and fell in the range from 0.5 to  $0.9 \mu\text{s}$ .

The data from the DLS experiments were analyzed by the heterodyne method based on DLS theory for a non-ergodic medium as described in Section 2.

## 4. Results and discussion

### 4.1. The effect of crosslink density

The experimental results from static light scattering from selected poly(AAm-co-AMPS) gels with different crosslink densities are presented in Fig. 1(a) and (b). The time-averaged light scattering intensity,  $\langle I(q) \rangle_T$  ( $\equiv \langle I \rangle_T$ ), is shown in the dependence on sample position in the gels. It should be noted that the scales in Fig. 1(a) and (b) are significantly different. The data for the gel with 2.5 mol% of MBAAM are presented in both parts of the figure for comparison.

Fig. 1(a) and (b) show that  $\langle I \rangle_T$  varies strongly with position in the sample. A general observation is that higher values of  $\langle I \rangle_T$  and larger amplitude of the variations in  $\langle I \rangle_T$  are attributable to gels with higher crosslink density. This implies that more inhomogeneities are incorporated in the gel structure with increasing crosslink density. The gel with 0.5 mol% of MBAAM shows very small variations in the scattered intensity, values of which are comparable to the values obtained for a solution of poly(AAm-co-AMPS), i.e. for the sample where no MBAAM is added (Fig. 2).

The variations in  $\langle I \rangle_T$  show the non-ergodic nature of poly(AAm-co-AMPS) gels, and an ensemble averaging is necessary. Such non-ergodicity is not observed in the

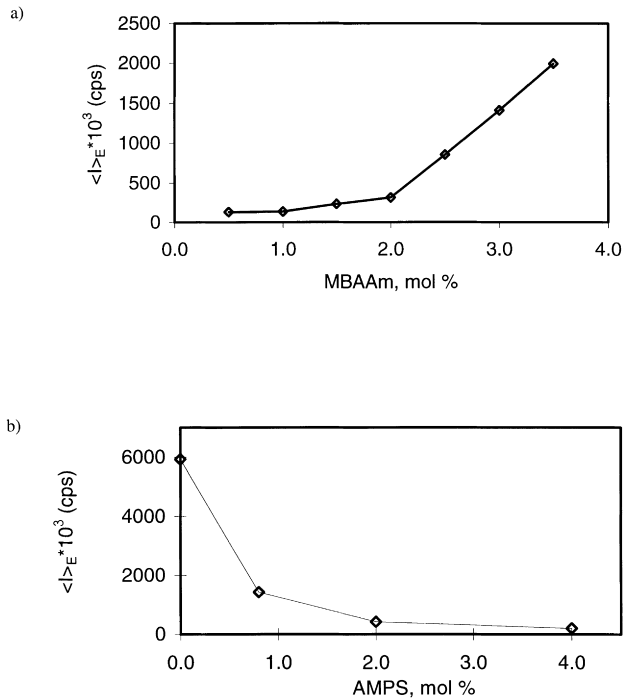


Fig. 3. Ensemble-averaged scattering intensity  $\langle I \rangle_E$  of poly(AAm-co-AMPS) gels: (a) dependence on the amount of MBAAm in the pre-gel solution; (b) dependence on the amount of AMPS in the pre-gel solution.

copolymer solution (Fig. 2). The dotted lines in Fig. 1(a) and (b) represent the ensemble-averaged scattered intensities  $\langle I \rangle_E$ .

The ensemble-averaged scattered intensity  $\langle I \rangle_E$  for poly(AAm-co-AMPS) gels of different crosslink density is presented in Fig. 3(a). The standard deviation of  $\langle I \rangle_T$  from the ensemble-averaged scattered intensity  $\langle I \rangle_E$  as function of  $\langle I \rangle_E$  is given in Fig. 4. The strong increase in  $\langle I \rangle_E$  at high crosslink densities, i.e. where the fraction of MBAAm is relatively high (>2 mol%), can be attributed to the enhanced formation of ‘crosslinking’ inhomogeneities in the gel network. To verify that speculation, i.e. to examine the origin of the enhancement of  $\langle I \rangle_T$  and  $\langle I \rangle_E$ , important information on the estimate of the fluctuating (thermal) part  $\langle I_F(q) \rangle$  of the scattered light intensity should also be known.

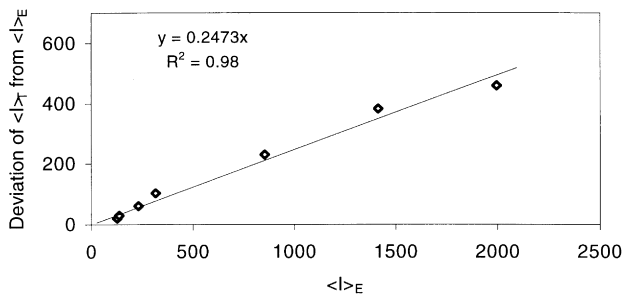


Fig. 4. Standard deviation of  $\langle I \rangle_T$  from the ensemble-averaged scattering intensity  $\langle I \rangle_E$ , as a function of  $\langle I \rangle_E$ .

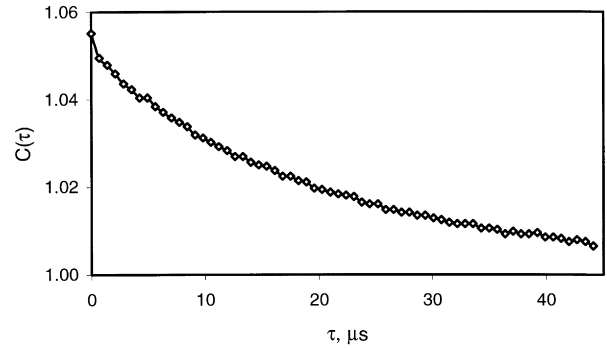


Fig. 5. Time-averaged intensity correlation curve for poly(AAm-co-AMPS) gel with 0.8 mol% of AMPS and 1.5 mol% of MBAAm.

As discussed above, information on the thermal concentration fluctuations in the gel network structure can be obtained by combining the static and dynamic light scattering results on the same gels, as described by Eq. (6).

An example of a time-averaged correlation function,  $C(\tau)$ , obtained in a DLS experiment at one position of poly(AAm-co-AMPS) gel containing 0.8 mol% AMPS and 1.5 mol% MBAAm, is shown in Fig. 5. The horizontal axis is the time between sampled intensities in the correlation function, in evenly spaced increments equal to the channel width, which was in this case  $0.7 \mu s$ . The portion of the correlation curve that smoothly decays towards the baseline comprises the useful information related to network dynamics. The apparent diffusion

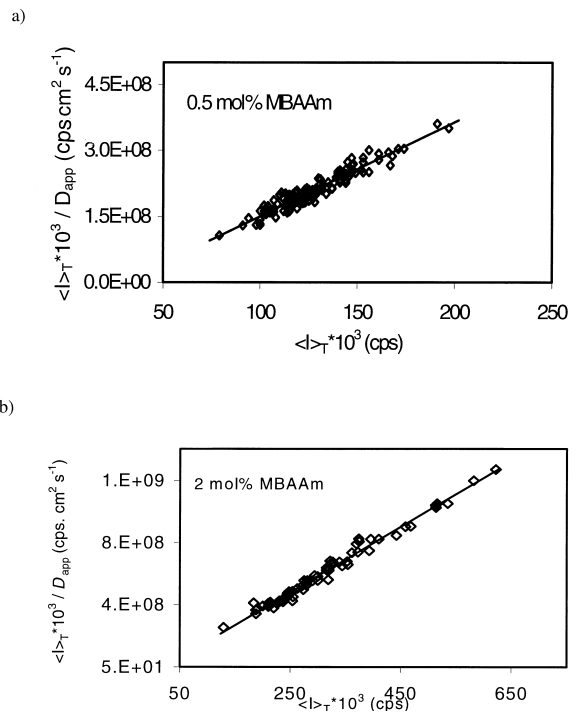


Fig. 6.  $\langle I \rangle_T / D_{app}$  as a function of  $\langle I \rangle_T$  for poly(AAm-co-AMPS) gels with the amounts of MBAAm indicated. The solid lines represent the linear fits.

Table 1

The intercepts and slopes for the LS data fitted with Eq. (6) (the linear regression analysis was performed with a weighting function of the form  $1/\langle I \rangle_T$ ), and calculated  $\langle I_F \rangle_T$  and  $D_c$ , for the poly(AAm-co-AMPS) gels with varying fractions of MBAAm

| MBAAm (mol%) | Intercept $\times 10^6$ ( $s\text{ cm}^{-2}$ ) | Slope $\times 10^7$ ( $\text{cps}/\text{cm}^2\text{ s}^{-1}$ ) | Correlation coefficient | $\langle I_F \rangle_T \times 10^3$ (cps) | $10^7 D_c$ ( $\text{cm}^2\text{ s}^{-1}$ ) |
|--------------|--|--|-------------------------|---|--|
| 0.5          | $2.13 \pm 0.06$                                | $-6.3 \pm 0.7$   | 0.98                    | $59 \pm 7$                                | $9.4 \pm 0.3$                              |
| 1.0          | $2.16 \pm 0.07$                                | $-5.7 \pm 1.0$   | 0.96                    | $53 \pm 9$                                | $9.3 \pm 0.3$                              |
| 1.5          | $2.13 \pm 0.04$                                | $-5.4 \pm 0.9$   | 0.93                    | $50 \pm 9$                                | $9.4 \pm 0.2$                              |
| 2.0          | $2.11 \pm 0.04$                                | $-5.1 \pm 0.9$   | 0.91                    | $49 \pm 9$                                | $9.5 \pm 0.1$                              |
| 2.5          | $2.10 \pm 0.03$                                | $-7.5 \pm 2.7$   | 0.92                    | $71 \pm 26$                               | $9.5 \pm 0.2$                              |
| 3.0          | $2.16 \pm 0.05$                                | $-9.6 \pm 6.7$   | 0.93                    | $89 \pm 62$                               | $9.3 \pm 0.2$                              |
| 3.5          | $2.18 \pm 0.11$                                | $-22 \pm 21$   | 0.94                    | $206 \pm 93$                              | $9.2 \pm 0.5$                              |

coefficient,  $D_{\text{app}} = 9.16 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , was evaluated from the decay of the curve in Fig. 5.

Fig. 6(a) and (b) presents examples of the plot of  $\langle I \rangle_T / D_{\text{app}}$  as a function of  $\langle I \rangle_T$  for poly(AAm-co-AMPS) gels with varying amounts of MBAAm, as indicated on the graphs. The data can be fitted with a linear equation of the form of Eq. (6), and the solid lines in Fig. 6 are best-fit lines. Estimated values of  $\langle I_F \rangle_T$  and  $D_c$  were obtained from linear regression analysis with the reciprocal of  $\langle I \rangle_T$  as the weighting function. Table 1 gives the intercepts and slopes, and the estimated values for the fluctuating component of the time-averaged light scattering  $\langle I_F \rangle_T$  and collective diffusion coefficients  $D_c$ .

From Fig. 6 and Table 1 it is apparent that with increasing fraction of MBAAm the range of the probed  $\langle I \rangle_T$  values is wider and the uncertainty in determining  $\langle I_F \rangle_T$  becomes more pronounced. This is clearly shown in Fig. 7(a) (right axis). It seems that, within the limits of error,  $\langle I_F \rangle_T$  does not

vary significantly with the molar fraction of MBAAm. This observation is in agreement with the findings of other authors [6]. It seems that thermal concentration fluctuations, represented by the  $\langle I_F \rangle_T$ , are not affected by the presence of the crosslinks, at least in the range of MBAAm contents that were investigated. The left axis on the graph in Fig. 7(a) represents the fraction of the thermal (dynamic) fluctuations  $\langle I_F \rangle_T$  in the ensemble-averaged light scattering intensity  $\langle I_E \rangle$ . The value of  $\langle I_F \rangle_T / \langle I_E \rangle$  strongly depends on the crosslink density, and is a decreasing function of the crosslink density. The implication is that the very strong excess of scattering intensity at high crosslink density is primarily due to static-structure inhomogeneities. The scattering results indicate that superstructure of the gel changes depending on the amount of crosslinking agent present. In addition, it may be that the hydrophobicity of MBAAm enhances the formation of polymer-dense regions in the gel structure leading to a microscopic spinodal decomposition [11]. However, the strong enhancement of scattering intensity with increase of crosslink density is also observed in gels prepared by other methods, for example by end-linking of polymer chains [27,28]. It was shown [1] that even in the idealized case of a ‘perfect’ chemical structure, different topological disorders might exist depending on the synthesis details.

Using the methods developed to date, and the one adopted here, it is possible to distinguish between the dynamic thermal concentration fluctuations and ‘frozen-in’ static superstructure. However, it is not possible to distinguish between the ‘quenched’ static structures due to crosslinking inhomogeneities and those due to disorder in the topology.

The dynamics of poly(AAm-co-AMPS) can be described by the collective diffusion coefficient  $D_c$ , obtained from the DLS experiments. Values of  $D_c$  for gels having 0.8 mol% of AMPS, and varying amounts of crosslink agent MBAAm are given in Table 1 and graphically presented in Fig. 8(a). It is apparent that  $D_c$  is independent of the crosslink density, in the investigated range of MBAAm fractions. The crosslinks do not, therefore, affect the relaxation of the polymer chains in the network of the poly(AAm-co-AMPS) gels. This behavior of the charged gels is different from that of neutral gels, where it was found that  $D_c$  is an increasing function of the crosslink density [6].

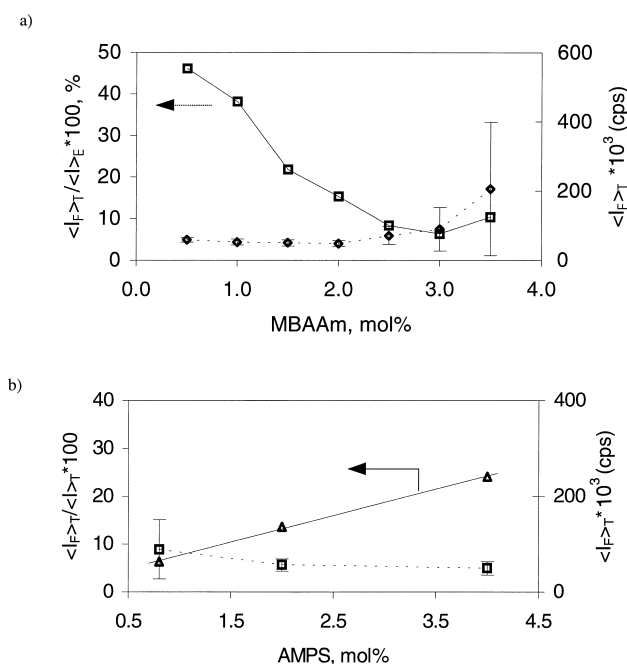


Fig. 7. Dependence of the dynamic concentration fluctuations  $\langle I_F \rangle_T$  and the ratio  $\langle I_F \rangle_T / \langle I_E \rangle$  on the fraction of (a) MBAAm and (b) AMPS used in the poly(AAm-co-AMPS) gel synthesis.

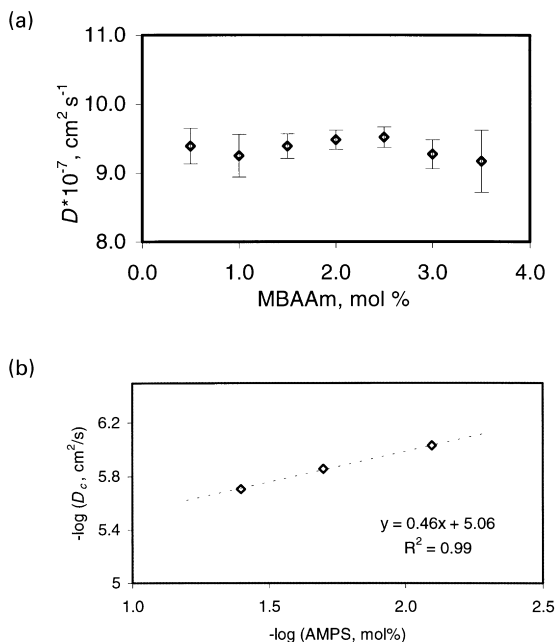


Fig. 8. (a) Crosslink density and (b) amount of AMPS dependence of the collective diffusion coefficient  $D_c$ , for the poly(AAm-co-AMPS) gels.

The correlation length,  $\xi$ , can be estimated from  $D_c$  values according to the relationship (based on the Stokes–Einstein equation):

$$D_c = kT/(6\pi\eta\xi) \quad (7)$$

where  $\eta$  is solvent viscosity (0.7975 cp for water at 30 °C). Since  $D_c$  is constant, within experimental error, for the gels investigated, the value for the correlation length is also constant. The calculated mean value is  $\xi = 29.6 \pm 0.3 \text{ \AA}^{-1}$ .

Recently Panyukov and Rabin have given a theory [29] for the structure factor of gels,  $S(q)$ . They have shown that  $S(q)$  consists of a contribution from the thermal (fluctuating) part and from static density inhomogeneities, and that  $S(q)$  is a complex function of a set of parameters related to the state

of gel preparation, and a set of parameters related to the conditions at observation. Their theory has been extended to weakly charged gels [21] (RP theory). Shibayama and co-workers analyzed the RP theory, and theoretically and experimentally predicted the dependence of the scattering function on the crosslink density [9,30]. They found that  $S(q)$  is a complex function of the crosslink density with an inflection at a certain set of experimental conditions. Such conditions for the inflection in the crosslink density dependence were not considered here.

#### 4.2. The effect of comonomer composition

For weakly charged polymer chains a small variation in the amount of ionizable group is expected to modify strongly the properties of the system. The effect of changing the composition of poly(AAm-co-AMPS) gels has been shown to be drastic in terms of gel swelling properties [20].

Fig. 9 shows the experimental results of static light scattering for poly(AAm-co-AMPS) gels with varying amounts of charged comonomer AMPS, and a constant amount of crosslinking agent MBAAm equal to 3 mol%. The time-averaged light scattering intensity  $\langle I \rangle_T$  varies randomly with position within the gel sample. The amplitude of the observed variations in  $\langle I \rangle_E$  decreases with increase in the amount of AMPS, indicating the presence of fewer inhomogeneities in the gel network structure. As before, the dotted lines in Fig. 9 denote  $\langle I \rangle_E$ .

The strong dependence of  $\langle I \rangle_E$  on the amount of charges on the polymer chains in poly(AAm-co-AMPS) gels, is shown in Fig. 3(b).  $\langle I \rangle_E$  decreases rapidly with increase of the amount of AMPS, to the extent that with 4 mol% of AMPS in pre-gel solution, the ensemble-averaged light scattering intensity  $\langle I \rangle_E$  drops to the value comparable to  $\langle I \rangle_T$  for the copolymer solution. The  $\langle I \rangle_T$  values for the gel with 0 mol% of charges were extremely high, at the limit of the linear response of the detector, and they could not be appropriately analyzed. The ensemble-averaged value is used in Fig. 3(b) to enhance the general trend of the effect of the charges in the system.

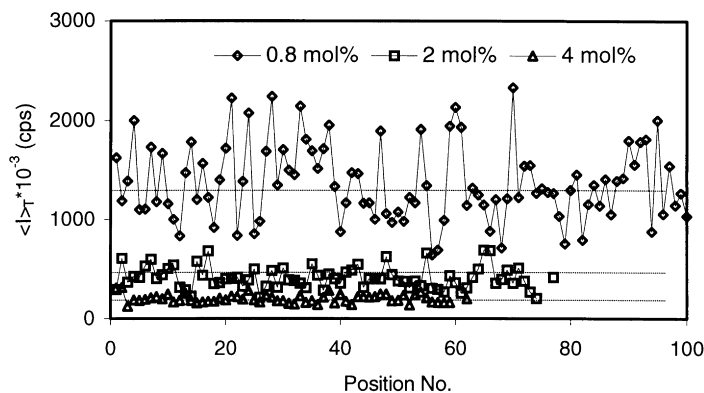


Fig. 9. Time-averaged light scattering intensity  $\langle I \rangle_T$  at various sample positions for poly(AAm-co-AMPS) gels with different amounts of AMPS as indicated on the graph, and constant MBAAm content of 3.0 mol%. The dotted lines represent the ensemble average of light scattering intensity  $\langle I \rangle_E$ .

Table 2

The intercepts and slopes for the data in Fig. 3 fitted with Eq. (7) (the linear regression analysis was performed with a weighting function of the form  $1/(I_T)$ ); and calculated  $\langle I_F \rangle_T$  and  $D_c$ , for the poly(AAm-co-AMPS) gels with varying fractions of AMPS, and 3.0 mol% of MBAAM

| AMPS (mol%) | Intercept $\times 10^6$ (s cm <sup>-2</sup> ) | Slope $\times 10^7$ (cps/cm <sup>2</sup> s <sup>-1</sup> ) | Correlation coefficient | $\langle I_F \rangle_T \times 10^3$ (cps) | $10^7 D_c$ (cm <sup>2</sup> s <sup>-1</sup> ) |
|-------------|---|--|-------------------------|---|---|
| 0.8         | $2.16 \pm 0.05$                               | $-9.6 \pm 6.7$   | 0.93                    | $89 \pm 62$                               | $9.3 \pm 0.2$                                 |
| 2.0         | $1.46 \pm 0.02$                               | $-4.8 \pm 0.9$   | 0.93                    | $66 \pm 13$                               | $13.7 \pm 0.2$                                |
| 4.0         | $1.02 \pm 0.04$                               | $-2.5 \pm 0.7$   | 0.96                    | $50 \pm 14$                               | $19.7 \pm 0.7$                                |

The enhancement of the scattered intensity with decrease in the fraction of charges on the chains was expected. For gels the compressional osmotic modulus  $K_{os}$  is directly proportional to the osmotic pressure of the gel (Eq. (6)). It has been shown [28] that, in the case of charged gels,  $K_{os}$  is the main contribution to the longitudinal osmotic modulus  $M_{os}$ , particularly at a fraction of charges larger than a few percent. Since  $M_{os}$  is inversely proportional to the intensity of the scattered light [28], the higher the osmotic pressure the lower the intensity of the scattered light will be.

The slopes and intercepts, and corresponding values of  $\langle I_F \rangle_T$  and  $D_c$ , obtained by plotting  $\langle I \rangle_T / D_{app}$  versus  $\langle I \rangle_T$ , are shown in Table 2.

Fig. 7(b) shows the dependence of dynamic concentration fluctuations  $\langle I_F \rangle_T$  and the ratio  $\langle I_F \rangle_T / \langle I \rangle_E$  on the fraction of AMPS in the poly(AAm-co-AMPS) gels. The figure suggests that, to a first approximation, the dynamic concentration fluctuations  $\langle I_F \rangle_T$  are independent of the fraction of charges. By contrast, the ratio  $\langle I_F \rangle_T / \langle I \rangle_E$  is a linearly increasing function of the amount of AMPS present in the gel, implying that increase of the amount of charges considerably suppresses the formation of static, frozen-in structures in the gel network. In other words, the structure inhomogeneities, and particularly the static-structure inhomogeneities, can be controlled by the osmotic properties of the network.

The effect of the molar fraction of AMPS in poly(AAm-co-AMPS) gel on the gel network dynamics, is shown in Fig. 8(b). The collective diffusion coefficient,  $D_c$ , was found to increase with increase in the fraction of AMPS in the gel. The dependence of  $D_c$  on the proportion of AMPS can be described by a power law with an exponent 0.46, obtained from the slope of the best-fit line in Fig. 8(b). The exponent is larger than the theoretically predicted exponent of 1/3, where  $D_c$  should scale with the degree of ionization  $i$  as [28]:  $D_c \sim c^{1/2} i^{1/3}$ . The deviation is slightly larger than that observed for poly(acrylic acid) gels [28], where the deviations are found to be dependent on polymer concentration  $c$  (exponents 0.42–0.27 for polymer concentrations  $c = 5 \times 10^{-3}$ – $15 \times 10^{-2}$  g cm<sup>-3</sup>).

The correlation lengths,  $\xi$ , estimated from obtained  $D_c$  values are 29.8, 20.0 and 14.1 Å for the poly(AAm-co-AMPS) gels with 0.8, 2 and 4 mol% of AMPS, respectively.

## 5. Conclusion

It has been realized recently that spatial inhomogeneities

of the gel network structure are intrinsic to polymer gels, and are a direct consequence of the gel preparation method as well as conditions at observation (or usage). Knowing how to define and control the extent of such structural inhomogeneities has become a new challenge.

To date, a limited number of polyelectrolyte gels have been investigated in relation to their structural inhomogeneities. LS experiments performed in the present study showed that poly(AAm-co-AMPS) gel superstructure can be decomposed into two contributions, static inhomogeneities and dynamic concentration fluctuations, in agreement with recent theories. The results revealed that the formation of large-scale static inhomogeneities is significant in the poly(AAm-co-AMPS) gels with very low fraction of charged comonomer and high crosslink density. A small increase in the proportion of AMPS in the copolymer gel increases the osmotic pressure considerably, and suppresses static network inhomogeneities.

The dynamics of poly(AAm-co-AMPS) gels was found to be independent of the crosslink density, while the increase in AMPS proportion in poly(AAm-co-AMPS) gel amplifies the gel dynamics.

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