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Fast internal dynamics in polyelectrolyte gels measured by dynamic light scattering

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Summary

Dynamic light scattering was used to investigate the dynamics of sodium poly(styrene sulfonate) and fully neutralized poly(acrylic acid) gels as a function of the degree of swelling and weight ratio of cross-linking agent. It was shown that the collective diffusion coefficient increases with increasing degree of swelling and that the diffusion coefficient shows stronger concentration dependence than predicted by scaling arguments. For gel samples measured at the swelling equilibrium, the diffusion coefficient increases with increasing gel concentration for both gel systems.

Introduction

Cross-linked polymer gels are common in much of our everyday surroundings, such as in training shoes or contact lenses. Recently, they have also been used as model substances for "smart" materials, which can undergo volume and shape transitions due to changes in external conditions. Examples include pH and temperature sensitive gel systems, as well as those responding to changes in electric field strength or salt concentration [1-4]. The change in gel volume as controlled by different external parameters has been the subject of many studies since this also makes the gels interesting for applications such as artificial muscles, biosensors, or as in vivo drug carriers [5-7].

Though the number of applications has increased during recent years, there is still a need for a more detailed understanding of the properties of gel systems, both concerning structure and dynamics. Many studies have been devoted to a problem how different gel materials respond to varying external parameters [1, 3, 4, 8-12]. The typical example being N-isopropylacrylamide gels, where the hydrophobic side groups induce a phase transition and a volume collapse above a critical temperature [13]. Other types of gels such as polyelectrolyte gels are sensitive to salt concentration and pH, depending on the properties of ionic groups which have been the subject of a number of studies, both theoretical [14-16] and experimental [17-20].

An important experimental method for studying polymer system is dynamic light scattering (DLS) [21-23] which provides information about dynamic properties on variety of length scales [24]. Dynamic light scattering studies of sol-gel systems have shown that on passing through the gel point from sol to gel, the character of the light scattering changes; the system can no longer be considered to be ergodic [25-27], at least not with respect to the motion of the polymer chains in the gel. Evaluation methods of DLS data takinginto account the non-ergodicity in light scattering experiments have been put forward by Geissler [28, 29] and Pusey [30-32]. A comparison of these methods can be found in the thesis of Fang [33]. The source of the non-ergodic behavior of polymer gels is their inherent heterogeneity [34, 35].

The frequently investigated gels of week acids were those of poly(acrylic acid) (PAA) gels. Schosseler et al. [36], investigated the structure and determined the diffusion coefficient for slightly charged unswollen cross-linked poly(acrylic acid) (PAA) gels by using both small angle neutron scattering (SANS) and DLS as a function of dissociation degree, α. The results have been satisfactorily explained using a model for microscopic phase separation in amphiphilic networks [37]. For small α, the cooperative diffusion coefficient, D, was found to behave in the same way as for neutral gels (D increased with concentration) while for large α D decreased with increasing polymer concentration.

In a subsequent paper [38], the same group investigated both unswollen and fully swollen gels using DLS and swelling kinetic experiment to determine the cooperative diffusion coefficient. For the fully swollen gels, the diffusion coefficient increased with increasing degree of swelling, i.e. with a decreasing gel concentration, opposite to that of neutral gels, but in line with scaling theory [30, 40]. The increase of the diffusion coefficient with increasing degree of swelling was however much larger than predicted by theory.

Milimouk et al. [41] measured swelling pressure and the collective diffusion coefficient as a function of the degree of swelling in two series of salt-free neutralized polyelectrolyte gels, poly(acrylic acid) and poly(acrylamide-acrylic acid). The values of D measured by kinetics of macroscopic deswelling were found to be in reasonable agreement with those measured by DLS. The diffusion coefficient increased with increasing degree of swelling.

Contrary to polyelectrolyte solutions [42], gel systems of strong electrolytes, such as poly(styrene sulfonate) (PSS) have been relatively less studied. Recently, the kinetics of gel swelling/deswelling for microgels of PAA and PSS [43] was published .

Since only few experiments seem to have been designed to investigate the dynamic properties of fully ionized polyelectrolyte gels we have decided to investigate mainly the effect of both swelling and cross-linking density on the short time dynamic properties of fully neutralized poly(acrylic acid) and poly(styrene sulfonate) by DLS using a fast correlator. In section 2 we describe the method of synthesis, sample preparation, and data analysis. In section 3 the results are presented and discussed and we end with some conclusions.

Experimental

Preparation of gel samples

The poly(acrylic acid) gel was synthesized using acrylic acid as monomer with methylene bis-acrylamide as cross linker and with N,N,N',N'-tetramethylethylenediamine (TEMED) and ammonium persulfate as accelerator and initiator, respectively. All ingredients were mixed in water and the relative amounts were approximately: 2.500 g acrylic acid, 0.015 g TEMED, 0.024 g ammonium persulfate, 19.960 g water;

the weight ration of cross-linker to PAA monomer, f_{cr}, was varied between 0.025 and 0.05 g.

The gel samples were prepared in test tubes with 1 cm diameter. After polymerizing over night at 65 ºC, the gels were removed from the test tubes and neutralized in 0.6 M NaOH. The neutralized and slightly swollen gels were washed out in MilliQ-water for several days and the water was changed at least five times. The amount of water was 7 dm^3 each time. The volume increase was about 100 times; it is believed that all non-trapped sol was removed from the gel during this process.

The poly(styrene sulfonate) gels were prepared in a similar way, using sodium styrene sulphonate as the monomer and a nitrogen atmosphere during the polymerization process. The relative amounts were in this case: 4.0 g sodium styrene sulfonate, 0.015 g TEMED, 0.024 g ammonium persulfate, 20.0 g water while the amount of cross-linker in this case was varied between 0.191 to 0.487 g. The PSS-gels, however, were more difficult to prepare and the conversion polymerization was probably not completed since f_{cr} value had to be very high (6-14%) for preparation of relatively week gels. Generally, they were also more fragile and difficult to handle.

Preparation of the light scattering samples was done by punching out a piece of the swollen gel, small enough to fit in the measuring cell. After drying the piece of gel slightly until it could slide into the cell, a small amount of MilliQ water was added to the cell to let the gel re-swell. Then, the cell was closed and the sample left to homogenize for 1 week. Different swelling ratios were obtained by drying the fully swollen gel for different periods of time before sample preparation. To determine the swelling ratio, the mass of the gel in the measuring cell was compared to the mass of the same piece after complete drying. Assuming that the volumes of polymer and water are approximately additive quantities, a relative degree of swelling, r_s, could be computed. Since this last step destroys the samples it could only be done after the light scattering measurements had been completed. The concentration of the gel samples, c_g, is given in weight percent and was obtained in the same manner by comparing the weight of the dry samples with the weight of the swollen sample.

Dynamic light scattering (DLS)

The dynamic light scattering measurements were performed using a polarized HeNe laser (35 mW, 632.8 nm), a motorized goniometer, and an ALV-6000 multiple tau digital correlator. The fast option of the correlator enabled measurements of intensity time correlation functions with a shortest delay time for the poly(acrylic acid) of 25 ns, while for the poly(styrene sulfonate) a new version of the correlator was used with a lower time limit of 6.25 ns. These are all an order of magnitude shorter than in earlier experiments [41].

Since permanent static structural inhomogeneities occurred in the gels, the ensemble-averaged correlation functions were obtained with a rotation unit manufactured by ALV (GmbH) and a non-ergodic average procedure of the correlator. The number of short measurements used to compute each average correlation function was about 30, and the results showed good consistency. The duration of measurements was about 900 seconds.

The analysis of the correlation function was done using the program GENDIST [44], which uses the algorithm REPES [45] to perform the inverse Laplace transformation. The result of the analysis is a distribution of relaxation times, $A(\tau)$. In general, $\mathrm{A}(\tau)$ consists of several peaks representing individual dynamic processes. The relaxation time τ of a dynamic process (or its relaxation rate $\Gamma = 1/\tau$) is then obtained as the first moment of the corresponding peak in the distribution. If the observed process is diffusive, the relaxation rate, Γ, is related to the apparent diffusion coefficient, D_A, by [24] the relation $\Gamma = D_A q^2$, where q is the scattering vector; $q = 4\pi n \sin(\theta/2) / \lambda$ with n the refractive index of the solvent, λ the wavelength of the incident light, and θ the scattering angle.

The average diffusion coefficient, D, was finally obtained from about ten D_θ values measured at several scattering angles. Throughout the paper the results are presented in terms of the average diffusion coefficient, D.

Results and discussion

A typical distribution of relaxation times given in Fig. 1 is dominated by the fast mode, which in this particular case is about 6 μs. In addition to the fast mode, slower modes are sometimes seen at longer relaxation times.

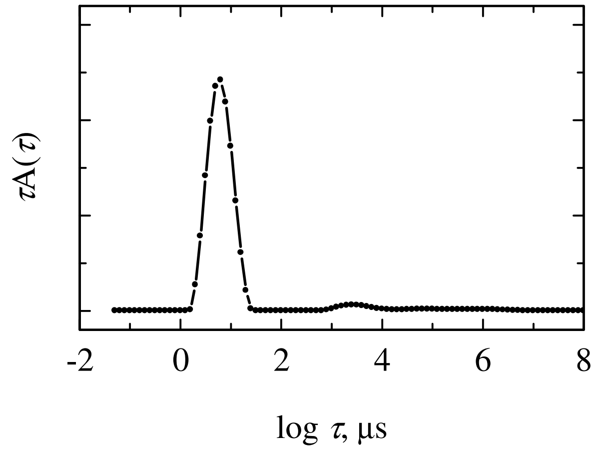

Figure 1. Distribution of relaxation times evaluated from the ensemble-averaged correlation function measured on poly(acrylic acid) gel prepared with 1.5 wt.% of cross-linker at a low swelling ratio. The correlation function was measured 2.5 hours at an scattering angle of 100° and at room temperature.

The fast mode is diffusive since its relaxation rate has been found to be a linear function of q^2 in all cases. The second mode probably results from a diffusion of the sol that was not removed from the gel during the washing procedure [33]. The fast mode could, in turn, be interpreted as the collective diffusion mode due to concentration fluctuations by the coupled diffusion of polymer segments and counter ions [46], which relax by movement of polymer chains and counter ions. The frozen-in static structural inhomogeneities determine the static light scattering contribution to the total scattered light responsible for heterodyning.

Varying the degree of swelling

The diffusion coefficients are shown as a function of gel concentration c_g for PAA-gels with f_{cr} = 1, 1.5 and 2 % and for PSS-gels with f_{cr} = 10 and 14% in Figure 2.

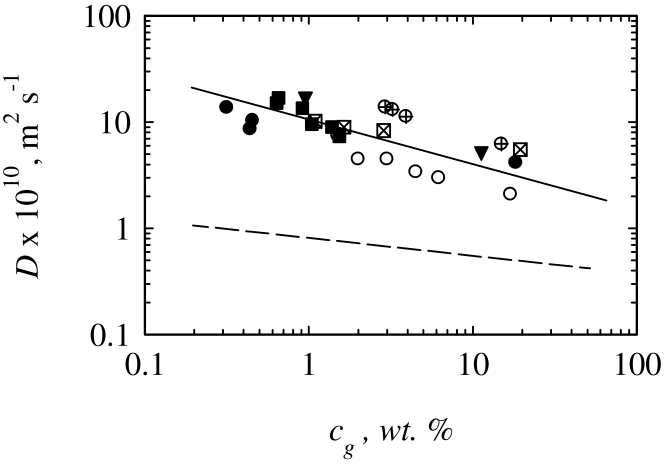

Figure 2. Diffusion coefficient, D, plotted as a function of concentration for three PAA gels with 1 (●), 1.5 (■), 2 (▼) wt. % of cross-link fraction and for two PSS gels with 10 (⊕) and 14 (☒) wt. % of cross-link fraction. The open symbols (o) denote data reproduced from ref. [41] (PAA gel prepared with 8 mol. % of cross-link fraction). The slope of the full line is -0.50. The broken line is a guide to the eye that that has a slope of -0.166 corresponding to the expected theoretical exponent [20].

The open symbols in Figure 2 represent earlier results obtained by Millimouk et al. [41]. The diffusion coefficients are also close to what has been observed in other studies of a similar gel system, D = 10^{-10}-10^{-9} m^2s^{-1} [38]. From Fig. 2, it is seen that the diffusion coefficient decreases with increasing concentration. The diffusive motion that corresponds to the fast relaxation process thus becomes faster as the gel network is swollen.

The change in diffusion coefficient with swelling of the polymer network has recently been analyzed using scaling theory [20, 41]. Assuming $D \sim c^{-a}$ and using scaling arguments it was found that the diffusion coefficient should change as $c^{-1/6}$. Thus, the diffusion coefficient in swollen polyelectrolyte gels indeed should decrease with increasing concentration.

In order to check these theoretical predictions we have fitted the experimental data in Fig. 2 to a straight line of which the slope describes the exponent -a. The average a is 0.5 ± 0.2 which is a value higher then the theoretical one (1/6) represented by a dashed line in Fig. 2. Although the diffusion coefficient also depends on the cross-linking density (see below), the value of the exponent $a \approx 0.5$ does not, within experimental accuracy, change much with f_{cr} and a type of polyelectrolyte gels under investigation.

Varying f_{cr} value

Besides the change of the diffusion coefficient with the degree of swelling, we also varied the weght ratio of cross-linking agent, f_{cr}, and measured the gels at maximum swelling (at swelling equilibrium). The relaxation rate was in all cases found to be a linear function of q^2, which indicates a diffusive process also for the most swollen gels. The diffusion coefficient, D, is shown as a function of equilibrium concentration c_g^e in Figure 3a. The data at maximum swelling correspond to different values of f_{cr}. For low values of f_{cr}, the network must expand more before reaching maximum

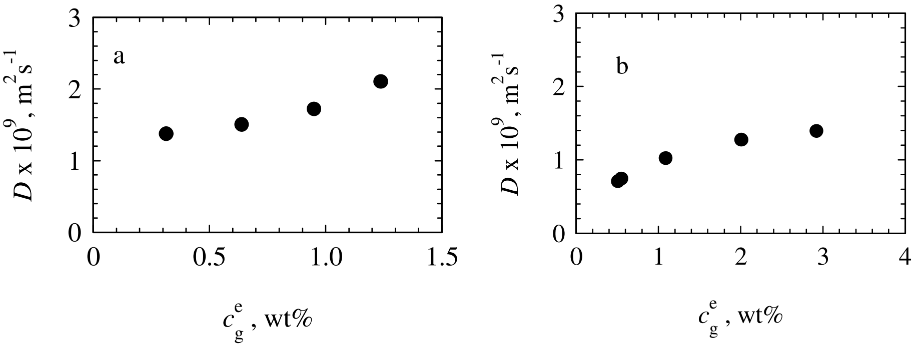

Figure 3. Diffusion coefficient, D, plotted as a function of concentration c_g^e for gels at swelling equilibrium; (a) for PAA gels with cross-linking density (from left to right) 1.0, 1.5, 2.0, and 2.5 %, (b) for PSS gels with cross-linking (from left to right) 6, 8, 10, 12 and 14 %.

swelling and the polymer concentration at equilibrium swelling thus decreases with decreasing f_{cr}. Similar data for the PSS gels are shown in Figure 3b.

It can be seen in Figures 3a and 3b that increasing c_g^e results in an increase of D and the coupled polymer – counter ion mode thus becomes faster. This result is in agreement with the relation [36], $D \approx \mathrm{k}Tc_g^e / f$, where k is the Boltzmann constant, assuming that the friction coefficient f is approximately independent of cross-linking density in the week gels under study.

The diffusion coefficient, D, was also found to be practically independent of temperature in the range from 20 to 80 °C.

Conclusions

We have investigated cross-linked polyelectrolyte gels at different values of f_{cr} and swelling r_s using dynamic light scattering.

With increased swelling of the network, the diffusion coefficient corresponding to the fast mode increased. The experimental results are in a qualitative agreement with prediction of scaling theory ($D \sim c^{-a}$). The experimentally determined value of $a \approx 0.5$ seems to be rather independent of f_{cr}, and in all cases, the a value was higher than that predicted by theory ($a = 0.166$).

At the maximum swelling of the gel, the diffusion coefficient increases with the increasing equilibrium concentration c_g^e. The diffusion coefficient, D, was also found to be practically independent of temperature in the range from 20 to 80 °C. To determine whether the scaling exponent a is really a universal constant further measurements have to be performed for different gel systems.

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