

Hydrogel suspensions as an electro-rheological fluid

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Abstract

Concentrated suspensions of swollen-in-water polyelectrolyte gels are shown to behave a new electro-rheological fluid. Without electric current the suspension apparent viscosity is high, while upon switching current the apparent viscosity drastically decreases. The change of apparent viscosity is due to the reversible contraction of the gel in the presence of an electric current. Under a 20–100 mA current, a suspension of sodium polyacrylate gel particles can decrease its apparent viscosity by more than 100 times. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The swelling and properties of polyelectrolyte gels can vary in response to the changes in the properties of the surrounding medium (pH, presence of ions, etc.) and/or external inputs. Being produced by the ton and used as superabsorbents for hygienic applications, polyelectrolyte gels possess a lot of other unique properties (for example, the ability to selectively absorb and/or release substances, to reversibly contract under electric current) which are still not enough studied and well understood from the point of view of fundamental science and not used in practice as well.

In the present work we show that a suspension of swollen-in-water hydrogel particles can behave as an electro-rheological fluid. To our knowledge there are no publication showing such a potential of hydrogel application. Usually, electro-rheological fluids are suspensions of solid particles with a high dielectric constant in a non-conducting liquid (oil). Without current the suspension is very fluid. Upon switching on the electric current, the particles orient and form a sort of a network which leads to a large viscosity increase [1]. One of the main problems for using such fluids in practice is that the particles are settling with gravity, destroying their electro-rheological properties. One way to overcome this difficulty is to use a solid matrix or a gel [2].

We propose here to use suspensions of swollen hydrogel particles without adding any solid particles. The idea is to take advantage of the reversible contraction of polyelectrolyte gels under electric current and to change and control the viscosity of the gel suspension by switching on and off the constant current. Looking quite “obvious”, such an idea of developing an electro-rheological fluid based on swollen-in-water hydrogel particles have never been reported before.

When using such an electro-rheological material, the target is to optimise the viscosity difference between the “on” and “off” states. The “on” state is controlled by the volume fraction of the particles (it is a suspension of contracted gel particles) which must be as low as possible to be close to the viscosity of the suspending medium (water). The “off” state is when the particles are fully swollen. To maximise the viscosity in this case means to fill all the space by particles, which are then transforming the material into a quasi-solid one. The investigations conducted here are in a confined environment (the gap of the rheometer) where the particles are filling all the space.

In this paper we will give the first results of the shear rheology of suspensions of swollen-in-water hydrogel particles under the presence or absence of an electric current and will demonstrate that these gel suspensions behave as electro-rheological fluids. In the first part the flow of the gel suspensions under shear will be reported. The flow of soft gel particles is an interesting subject in itself with only a few experimental results reported [3–5] and few theoretical interpretations. Here, we shall only show how the concentrated suspensions of swollen-in-water gel particles flow

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under shear when placed in a confined environment and discuss the apparent viscosity-concentration dependence of gel suspensions. In the second part, the hydrogel behaviour under electric current will be examined. Finally, we will demonstrate that a suspension of swollen-in-water hydrogel particles is an electro-rheological fluid, where the apparent viscosity can be controlled and significantly changed by the application of a constant electric current. As will be explained later, the viscosity measurements are not giving a true viscosity because of a large plug flow effect when the gel is highly swollen.

2. Experimental

2.1. Materials

The hydrogel used in this study was poly (0.75 acrylate–0.25 acrylic acid), cross-linked by N,N' -methylenebisacrylamide, degree of cross-linking 0.06% mole fraction with respect to the monomer, kindly provided by Atochem, a French company. The size of the dry gel particles is 0.1–0.2 mm with a maximal degree of swelling in water of about 600 g/g. The suspensions of gel particles swollen to different extent were prepared by simply mixing dry gel powder with a certain amount of distilled water. The concentrations were measured in weight per cent.

2.2. Methods

Both rheological and electro-rheological experiments were performed using a stress-controlled StressTech® rheometer, manufactured by Reologica Instruments. The flow of hydrogel suspensions under shear was studied in the parallel plate geometry for the concentrated suspension (gap 2 mm) and Couette cell (two concentric cylinders with a gap of 2 mm) for the dilute suspensions. The electro-rheological studies were performed in the parallel plate geometry (plate diameter 30 mm, gap of 2 mm). The electrodes were in stainless steel, so that neither corrosion, nor ion emission took place. We used a constant electric power generator “Delta Electronica” and an amperemeter for changing and controlling the current values, correspondingly.

As will be seen later, the size of a fully swollen gel particle is only slightly smaller than the rheometer gap size (this is not true when the gel particle is in a contracted state). This is done to maximise the viscosity difference between the fully swollen state where we expect the gel suspension to behave as a solid material and the collapsed state where the material is fluid. This is close to what would be found in a real application. It has the disadvantage, from a scientific point of view, of not allowing the measurement of a true viscosity since in the swollen state, a lot of the energy dissipation comes from the friction of the gel on the rheometer plates. In all the paper, the viscosity is apparent, being calculated classically assuming no surface friction and no plug flow.

Because of the gel size polydispersity the suspension viscosity decreases in time after beginning of shearing and then stays constant in 10–15 min. Thus both rheological and electro-rheological experiments were performed after 15 min of pre-shearing. The measurements were made from low to high shear rates. We also performed a few tests by measuring the suspension viscosity from high to low shear rates and we checked that within the experimental errors there is no difference with the viscosities measured at low-to-high shear rates.

3. Results and discussion

3.1. Correlation between hydrogel swelling degree and concentrations in suspensions of gel particles

There are three different concentrations that must be recognised in hydrogel suspensions. The first is the total polymer concentration in the suspension, that will be noted C . The second is the polymer concentration in the gel particle, noted C_{pol} . As far as the maximal degree of swelling is 600 g/g, the minimal $C_{\text{pol}} = 0.167\% = C_{\text{pol}}^*$. C_{pol} thus varies from 0.167 to 100%, when the gel is dry. The third concentration that is important is the gel particle concentration in the suspension, noted C_{part} . It can vary from zero (no gel in the suspension) to the maximum packing density which is close to one hundred per cent for the case of soft deformable gel particles.

When C is larger than C_{pol}^* , the particles fill the space with $C_{\text{part}} \sim 100\%$. The increase of C keeps C_{part} constant, but increases C_{pol} . In other words, the increase of the total polymer concentration above C_{pol}^* leads to the decrease of gel degree of swelling because of the lack of solvent. In this case there is no solvent (water) between the particles.

When $C < C_{\text{pol}}^*$, the particles are swollen at their maximum ($C_{\text{pol}} = C_{\text{pol}}^*$), thus there is a certain amount of free water around the particles which do not fill all the space. To summarise, the variation of the total polymer concentration in the hydrogel suspension either changes C_{pol} and keeps C_{part} constant when $C > C_{\text{pol}}^*$ (gel degree of swelling is lower than the maximal), or changes C_{part} and keeps C_{pol} constant when $C < C_{\text{pol}}^*$ (gel is swollen at its maximum).

3.2. Flow of hydrogel suspensions under shear (without electric current)

The flow of gel suspensions is shown in Fig. 1. The characteristics of the studied suspensions are given in Table 1. In order to be close to cases where these fluids may be used, the total polymer concentration is varied around C_{pol}^* , where in most of the cases (suspensions 1–5) the particles are filling all the space ($C_{\text{pol}} \sim 100\%$). In the preceding study on the similar hydrogel suspensions [5] we observed that when $C < 0.1C_{\text{pol}}^*$, the suspensions behave as Newtonian fluids. In this study the concentration range is $0.2C_{\text{pol}}^* < C < 3C_{\text{pol}}^*$. Fig. 1 shows that at $C > C_{\text{pol}}^*$ the suspensions are

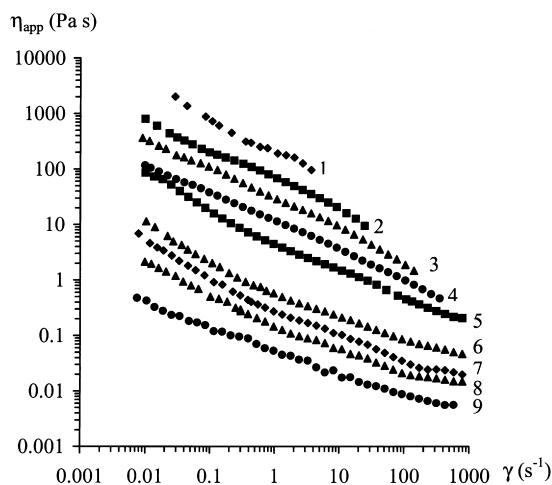


Fig. 1. Flow curves of the suspensions of hydrogel particles, figures correspond to the numbers of the suspensions, as listed in Table 1.

responding as quasi-solid bodies, with a viscosity almost proportional to the inverse of the shear rate. This reflects the fact that the dissipated energy is due to the friction of the quasi-solid suspension on the wall of the rheometer, due to the difficulty of one gel particle to pass around another one. We observed such concentrated suspension in a transparent rheometer and saw this effect. The larger is the concentration, the higher is the flowing stress. With the increase of the total polymer concentration above C_{pol}^* the gel particles become more and more “hard” since there is less and less water in the system. This also increases the flow stress by limiting the layer of water between the particles and the wall, and probably preventing particles to accommodate the deformation.

Fig. 2 shows that the apparent viscosity of the suspension, taken for a shear rate of 1 s^{-1} , is increasing with the total polymer concentration. The regime changes at $C = C_{pol}^*$ when the particles start to fill all the space. Below C_{pol}^* the viscosity increases rapidly because of the viscous dissipation due to particle–particle interactions. The viscosity curve below C_{pol}^* shows an asymptotic approach to infinity

Table 1

Characteristics of hydrogel suspensions: N is the number of each suspension, C is the total polymer concentration in the suspension, C_{pol} is the polymer concentration in the particle and C_{part} is the gel particle concentration in the suspension

No.	C (%)	C_{pol} (%)	C_{part} (%)
1	5.0	5.0	100
2	1.0	1.0	100
3	0.5	0.5	100
4	0.25	0.25	100
5	0.167	$0.167 = C_{pol}^*$	100
6	0.125	0.167	75
7	0.110	0.167	67
8	0.077	0.167	46
9	0.040	0.167	24

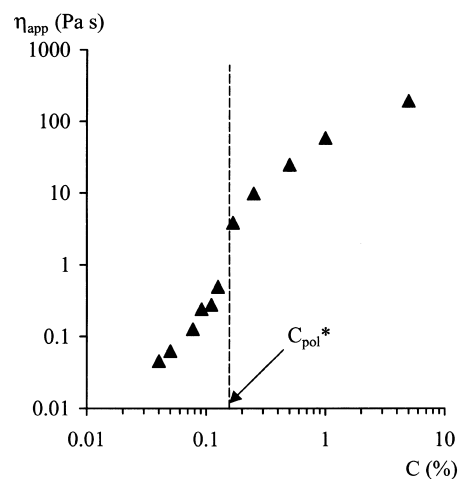


Fig. 2. Apparent viscosity-concentration dependence of hydrogel suspensions for an applied shear rate of $\gamma = 1 \text{ s}^{-1}$.

up to C_{pol}^* where it should be infinite for hard spheres. Above C_{pol}^* , the suspensions response as a rigid body with friction along the walls. The higher is the concentration above C_{pol}^* , the harder are the particles and the smaller is the amount of water that can be used for lubricating. The increase of viscosity above C_{pol}^* reflects the increase of wall friction.

3.3. Hydrogel behaviour under a constant electric current (without flow)

A polyelectrolyte hydrogel reversible contraction under a constant electric current has been reported in several articles (see, for example, a review [2]). When electrodes touch a swollen gel and a constant current is switched on, the hydrogel contracts and water is released. When the current is switched off, the gel swells again and this cycle can be repeated. This phenomenon is explained by the changes of the pH and/or ionic strength near the electrodes and inside the gel and is caused by the flow of mobile ions under current [2].

The contraction kinetics of a charged gel under electric fields was already reported in several publications (see, for example, Refs. [2,6–9]). In order to predict the viscosity changes of hydrogel suspension upon switching on and off the electric current we shall use the results obtained in Ref. [7] for a gel block based on cross-linked sodium polyacrylate. This approach is valid because the change in the suspension viscosity is based on the change of the gel particle size. In Ref. [7] it was shown that the amount of water released from the gel is proportional to the charge transported through it, at the beginning of the contractile process. To obtain this result, gel pieces of various initial sizes were placed between two electrodes always touching the sample. The decrease of the gel weight was measured as a function of the current and time. These results are shown again in Fig. 3 taken from Ref. [7]. It was later demonstrated [8] that the whole contraction kinetics can be described by the Faraday law written in the exponential form taking into account

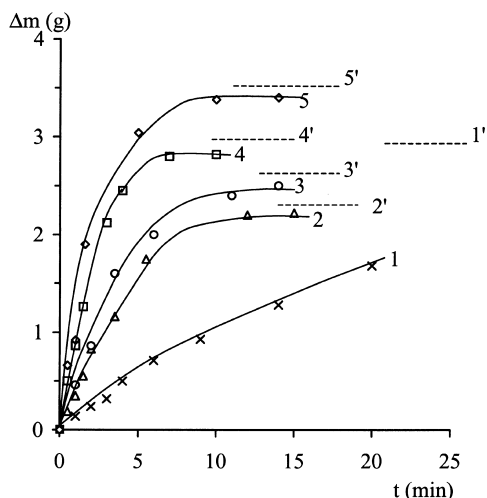


Fig. 3. Kinetics of hydrogel weight loss under constant electric current: 1.4 mA (1), 4.3 mA (2, 3), 8.3 mA (4, 5). The values of the initial gel weight m_0 are given by dashed lines and numbered in accordance to the contractile curves.

that under current the hydrogel degree of swelling is changing in time:

$$-\frac{dm(t)}{dt} = Q(t)M \frac{J}{C} \quad (2)$$

where $m(t)$ is the weight of the collapsing gel as a function of time t , $Q(t)$ the gel degree of swelling at a fixed time, $M = 94$ g/mol the molar weight of the sodium polyacrylate; J the electric current and C a constant.

The solution of this differential equation with the boundary condition $m(t)|_{t=0} = m_0$ (m_0 being the initial weight of a gel piece swollen at equilibrium in water) is:

$$\frac{m_0 - m(t)}{m_0} = \frac{\Delta m}{m_0} = 1 - \exp\left(-Q_0 \frac{M}{m_0 C} J t\right) \quad (3)$$

Q_0 being the hydrogel.

Using the results obtained in Ref. [7] the dependence of the weight change on the charge transported through the sample is presented in Fig. 4 in reduced co-ordinates $\Delta m/m_0$ versus Jt/m_0 . The experimental results obtained for various gel pieces of several weights under different current values fall on a single master plot. The constant $C = F/1.5$ (F being the Faraday constant) was calculated from the slope of the straight line when data are presented in a semi-logarithmic scale. Thus, the mass (or volume) change of a polyelectrolyte gel under a constant current can be described by the Faraday law written in the exponential form with a correction coefficient. We shall use this result for the following analysis of the electro-rheological behaviour of the suspension of swollen-in-water hydrogel particles.

3.4. Electro-rheological properties of hydrogel suspensions

Since the viscosity of gel suspensions is a strong function

of the total polymer concentration (or the volume fraction of hydrogel particles) and since hydrogel degree of swelling can be changed by application of a constant electric current, it was natural to investigate if the suspension viscosity can be changed under the electric field. Such experiments were performed in a plate–plate electro-rheological cell.

For most electro-rheological experiments we used hydrogel particles swollen at degrees lower than the maximal swelling in water (400 g/g), which means that there was no free water around the swollen particles. A constant shear stress of 10 Pa was applied and the changes of the suspension viscosity in time as a function of electric current were recorded. The examples of gel swelling/deswelling cycles are shown in Fig. 5a and b for electric current values of 20 and 80 mA, respectively.

At the beginning, without electric current, the suspension viscosity was more or less constant in time. As soon as a constant current was switched on during a given time (from point A to B, see Fig. 5a and b) the viscosity falls down quickly. The duration of the current application is shown on the curves near point A. The voltage applied being about 5–6 V at the beginning was changing in time because the hydrogel resistance changes under current.

Upon the current application the viscosity decreases immediately. We had to stop the current before the end of complete contraction because we found that above a certain contraction level, water started to release out of the gap. A better adapted cell is needed for a complete electro-rheological study. The data we present here were obtained before any water release from the gap.

As soon as the current was switched off, the gel was swelling in time. This was accompanied by a viscosity increase in time (from point B to point A, see Fig. 5a and b). The kinetics of gel swelling depends, generally speaking, on its molecular characteristics (cross-linking density), its morphology (specific surface) and size [10].

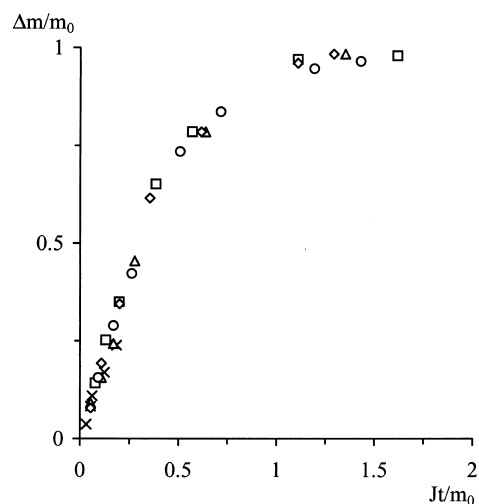


Fig. 4. Master plot of hydrogel contraction under a constant current (data taken from Fig. 3).

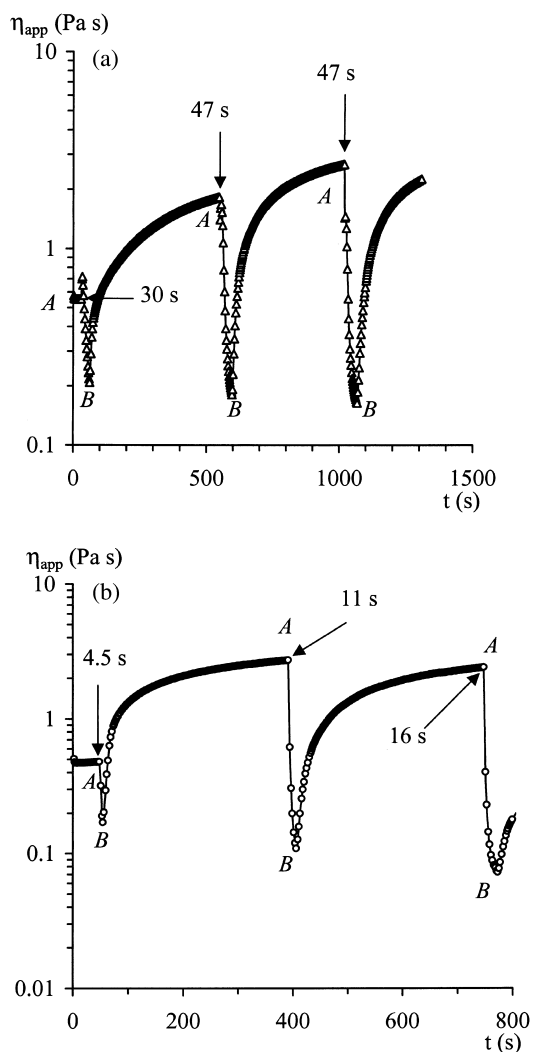


Fig. 5. Changes of the suspension apparent viscosity as a function of time and current switching on (point A) and off (point B) for several cycles. The initial stress was 12 Pa. The duration of current application is shown by arrows at the beginning of contraction. (a) Current strength of 20 mA; (b) current strength of 80 mA.

The cycle can be repeated several times for the same suspension (the stress being kept constant). In some of the cases the viscosity of the swollen gel suspension after the first cycle was higher than at the initial state without current. One possible reason could be as follows: being transformed under the electric current from sodium polyacrylate to a polyacrylic acid, the gel surface becomes adhesive (this is known for gels based on polyacrylic acid) and thus the suspension viscosity increases. However, if this is just an artefact or there are other reasons for such a viscosity increase is still an open question.

The contractile curves (Fig. 5a and b) show that the viscosity fall is more pronounced during the first seconds of current application. This is the consequence of the exponential dependence of the hydrogel weight change on the charge transported through the sample (see the section describing gel behaviour under a constant current).

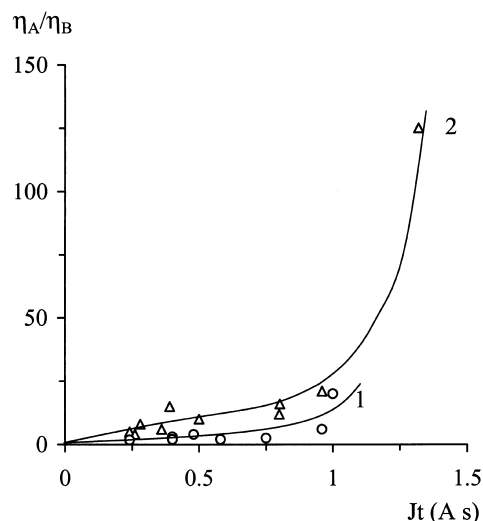


Fig. 6. Apparent viscosity difference as a function of the charge transported through the suspension: for the first (1) and for the second (2) current applications.

Because the change of the gel weight under current depends on the charge transported through the sample, the difference in viscosity η_A/η_B (η_A and η_B being maximal and minimal viscosities, correspondingly, at points A and B) also depends on the product of the current and time of current application. The results obtained for several cycles are presented in Fig. 6.

Two regimes can be distinguished: “the first step”, when the current was applied to the suspension for the first time (Fig. 6, curve 1) and “the second step”, when the current was applied to the same suspension for the second and further times. Certainly, for both the first and second steps η_B was measured before water was released out of the gap. This means that if the volume hydrogel + solution could be kept constant (in another set-up, for example, in an electro-rheological Couette cell), further increase of Jt should lead to higher values of η_A/η_B because of the significant viscosity fall below C_{pol}^* (see the section describing viscosity-concentration dependence of the gel suspension).

It is not very clear why the same charge transported through the gel causes a greater viscosity changes at second and subsequent current applications to the same gel suspension (compare curves a and b in Fig. 6). This cannot be probably explained only by the artefact of the particles “sticky surface” because of the contraction: η_A of the second step is higher than η_A of the first step. Also the values of η_B of the second step are lower than the ones of the first step. According to the electro-osmotic mechanism of hydrogel contraction [9], channels may be formed in the gel after once the current was applied. Then, during the following contractions, the water release could be easier.

3.5. Electro-rheological oscillatory test

In order to demonstrate that the type of deformation of a

hydrogel suspension does not influence its electro-rheological properties we performed a few electro-rheological tests in the oscillatory regime. The experiments were performed in the same way as for pure shear. Oscillatory shear was applied to the same suspensions of hydrogel particles swollen at 400 g/g. For each test a constant frequency (from 0.1 to 1 Hz) and a constant shear stress (from 30 to 50 Pa) was applied first without electric current. Under these conditions, after some pre-oscillating, hydrogel suspensions did not show viscosity dependence on time. Then the electric current of 20–80 mA was switched on and the changes of the suspension viscosity in time were measured. We recorded sharp viscosity falls as soon as current was switched on and the following slow viscosity increase when the current was switched off. Before water release from the gap, for the charge values up to 1 C the viscosity difference η_A/η_B was up to 15 times. Certainly, if keeping the volume of gel + released water constant, the viscosity difference should be greater. What we wanted to show here is that suspensions of hydrogel particles show electro-rheological properties not depending on the type of deformation.

4. Conclusions

The results reported here demonstrate that suspen-

sions of strongly charged hydrogel particles exhibit significant electro-rheological properties. We observed apparent viscosity changes up to 100 times caused by a charge of about 1 C transported through the gel with applied voltages of about 5–10 V. Using a better adapted cell, we feel that the viscosity fall can be much greater, up to 10,000.

This phenomenon may open new opportunities in the development of electro-rheological fluids or electrically driven smart materials.

References

- [1] Winslow WM. *J Appl Phys* 1949;24:1137.
- [2] Shiga T. *Adv Polym Sci* 1997;134:131.
- [3] Ishikura S. *Macromol Symp* 1996;101:115.
- [4] Frith WJ, Lips A. *Adv Colloid Interface Sci* 1995;61:161.
- [5] Budtova TV, Budtov VP, Navard P, Frenkel SYa. *J Appl Polym Sci* 1994;52:721.
- [6] Doi M, Matsumoto M, Hirose Y. *Macromolecules* 1992;25:5504.
- [7] Budtova T, Suleimenov I, Frenkel S. *Polym Gels Networks* 1995;3:387.
- [8] Budtova T, Suleimenov I. Unpublished results.
- [9] Starodubtsev SG, Khokhlov AR, Makhaeva EE. *Polym Bull* 1991;25:373.
- [10] Budtova T, Navard P. *Macromolecules* 1998;31:8845.