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Critical exponents in a percolation picture of the fluorescence quenching during the sol-gel transition

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Abstract. Herewith we report on the measurements of the time evolution of the fluorescence yield and the Rayleigh scattering, performed during the gelation process in the following solutions: gelatin in water, gelatin in a heavy water and agarose in water. Our results provide the experimental evidence of the universal power law, resulting from the percolation theory, which expresses the dependence of the fluorescence yield on the number of intermolecular bonds created during the sol-gel transition. The values of universal critical exponents present in this law are found to have the same values for all investigated materials.

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Introduction

The process of gelation has been described in terms of the percolation theory by a number of authors [1–10]. In view of this theory in the sol state molecules of the solute join into small aggregates, called clusters, which grow in size during gelation. The phase transition from the sol state to the gel state takes place, when small clusters link together and create one huge cluster, which fills most of the volume. The moment, at which this huge cluster appears for the first time, indicates the gel point. In the gel state the number of the finite clusters decreases in train of gelation, whereas the size of the huge cluster grows until all molecules are involved in its structure. The size of this huge cluster, called gel fraction, plays the role of the order parameter in the Landau theory of the second order phase transitions [3–5].

Recently we have applied the percolation theory [7] to explain the quenching of the fluorescence yield of the dye molecules embedded in the network of the gelling substance. We maintain that the reason of the fluorescence quenching is the nonradiative dissipation of the dye radiative energy into the vibrational modes of the molecular clusters. The nonradiative transition rates are functions of the cluster sizes [11]. The amount of the lost dye energy increases with the growth of the gel fraction. We have shown that dependence of fluorescence yield on the number of intermolecular bonds, responsible for the network formation, can be described by the power law, which reflects the second order type of the sol-gel transition.

The aim of this paper is to demonstrate, that the model proposed by us has the universal character and to check whether the critical exponents [3], present in the power law, depend on the type and the strength of the intermolecular bonds.

For this purpose we perform the measurements in three substances differing by the strengths of the bonds, and thus the dynamics of the network formation. As the experimental samples we have used two reversible physical gels: the gelatin dissolved in two different solvents, *i.e.* water and heavy water, and the aqueous solution of agarose. In all three cases the molecular network is linked by the hydrogen bonds. Gelatin is a biopolymer, a protein that is derived from naturally occurring collagen by denaturation process. In water it creates the temperature reversible weak physical gel [5,6]. In heavy water the hydrogen atoms in hydrogen bonds are being exchanged by deuterium [12], and the character and strength of the bonds significantly changes [13]. It is apparent in the dynamics of the gelation process, which proceeds much quicker than in a water solution and the resultant gel is much more rigid. Agarose is a polysaccharide derived from naturally occurring derivatives from seaweeds. It gels rapidly and creates the gel of a very high gel strength [14,15].

Aside to the fluorescence measurements we register the time evolution of the optical activity of the media, which is directly connected with the number of intermolecular bonds [16]. Eliminating time from both experimental results we can obtain the required plots describing the dependence of the fluorescence yield on the number of bonds. The critical exponents are obtained by the numerical fitting of the theoretical power law to the experimental curves.

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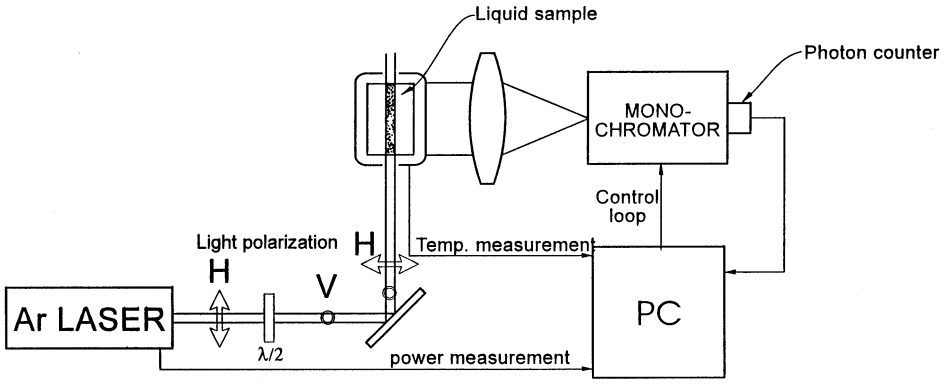


Fig. 1. The experimental set up.

Simultaneously we have applied the third experimental method, light scattering measurements, which have been widely applied for the gelation studies [2,8,9,17,18], also in the context of the percolation theory. Anyway those studies were performed mainly in the sol state, because the behaviour of the system in the sol state approaching the gel point is well described by the percolation theory. We have studied the time evolution of the scattered light intensity during all phases of the gel formation. Comparison of the obtained results with the optical activity measurements and application of the method of time elimination mentioned above allowed us to find the scattered light intensity as a function of the number of intermolecular bonds. On the base of the percolation theory we have found the power law expressing this dependence in the gel state.

Experiment

We have measured the time evolution of the fluorescence spectra and of the Rayleigh line wing during gelation of 3% gelatin in H_2O and in D_2O solutions and of 1% agarose in H_2O solution at the temperature $T = 22$ °C. The concentration of agarose was to be lower, because the process of gelation for higher concentrations was too rapid to be followed. The gelatin sample, from a pig skin, bloom test 150, was provided by the British Drug House Ltd., Poole, England. The agarose for electrophoresis sample was provided by E. Merck, Darmstadt, Germany. As the light source we have used the 100 mW power diode pumped Nd YAG CW laser at 532-nm wavelength. We have made the observations at the angle 90° with respect to the propagation direction of the incident wave. Two polarizations of the incident light have been considered: perpendicular (V) and parallel (H) to the plane created by propagation vectors of both incident and scattered light waves. The experimental set up and the polarization configurations are shown in Figure 1. The samples were kept for 1 h in the hot bath at $T = 50$ °C in the case of gelatin and at 80 °C in the case of agarose and then switched to the second bath at a lower temperature. The stabilization of the temperature was assured by use of a jacketed cell. The fluorescence and Rayleigh spectra, resolved by a 0.5-m monochromator, were acquired every 110 s by a photon-counting technique. The temperature was directly measured in the cell by a thermistor. The spectra, input power, temperature, and time of the individual measurements were registered simultaneously by the data acquisition system.

The results of our measurements are shown in Figures 2a–f. In the case of H polarization of the incident light at the angle 90° we detect only the depolarized light wave, whereas in the case of V polarization of the incident light the detected wave has the main component of the same polarization and it contains also the component of the changed polarization [19]. In all cases considered and at both polarizations of the incident light we observe the fall of the fluorescence yield in course of gelation, but the dynamics of the changes is completely different in each of the investigated materials. In the spectra corresponding to the V polarization we can see more water Raman peaks, which are not visible in the depolarized light. In the D_2O gelatin solution those peaks grow during gelation due to the deuterium-hydrogen exchange in the intermolecular hydrogen bonds. This phenomenon has been discussed by us elsewhere [13]. The Rayleigh wing is much stronger in the case of V polarization of the incident light. The intensity of the Rayleigh wing apparently increases in train of gelation, whereas this increase is much stronger in the case of the V polarization. Such an observation suggests that the density fluctuations, responsible for the polarized component of the scattered light, are the main reason of the Rayleigh scattering in gels [19,20]. Thus, for investigation of the fluorescence evolution we have chosen the results obtained at the H polarization, less perturbed by Rayleigh background changes. For investigation of the Rayleigh line evolution we have taken the results obtained at the V polarization.

The time evolution of the fluorescence yield is shown in Figure 3, which presents the time dependence of the integral fluorescence intensity for all studied solutions. The integral intensities have been calculated for spectra in Figure 2a–c by integrating the areas under the curves in the frequency range from 1 200 cm^{-1} to 2 200 cm^{-1}

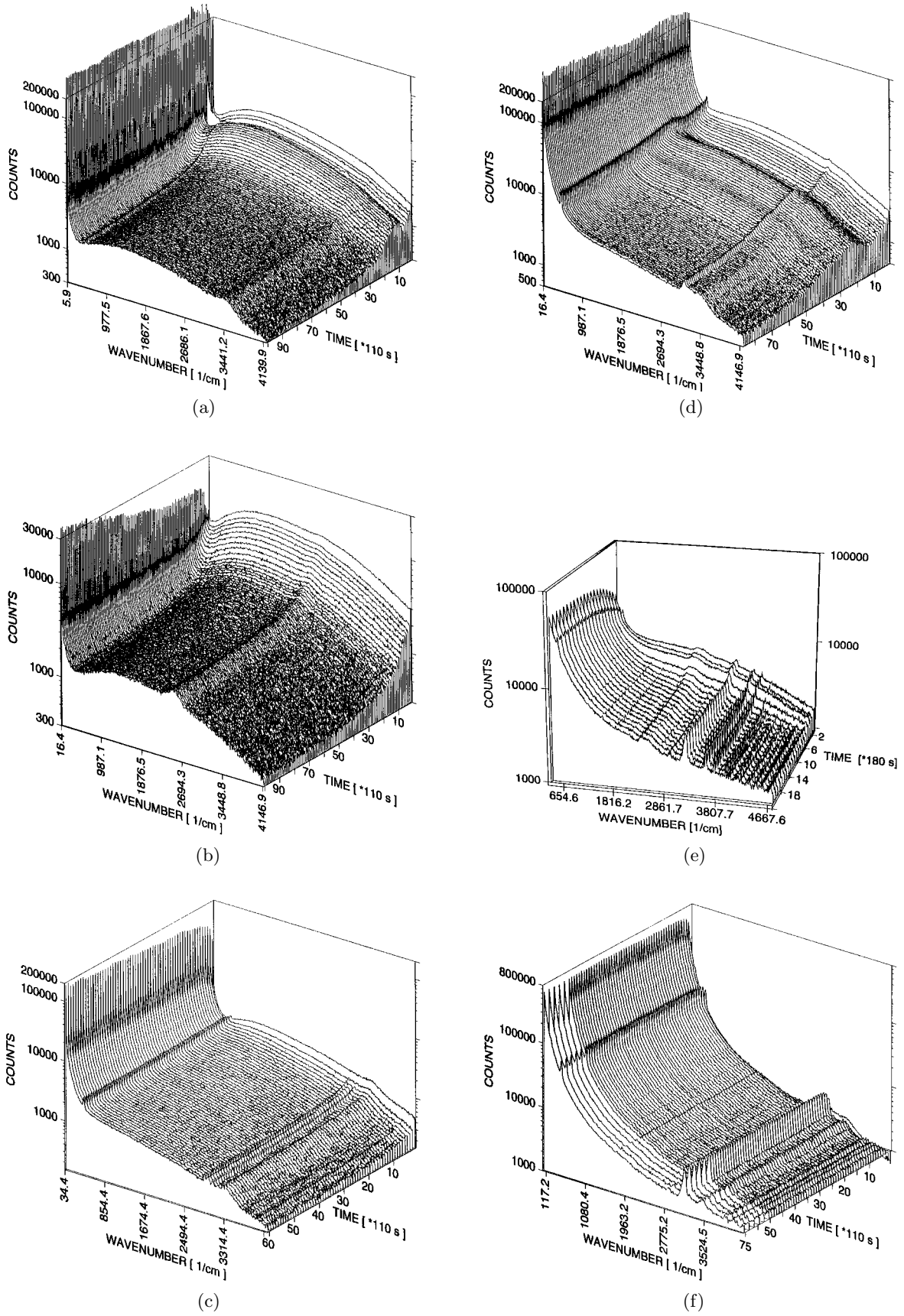


Fig. 2. Time evolution of Rayleigh and fluorescence spectra of: (a) and (d) gelatin in H_2O, (b) and (e) gelatin in D_2O, (c) and (f) agarose in H_2O. Plots (a), (b), (c) were taken at H polarization and plots (d), (e), (f) at V polarization of incident light.

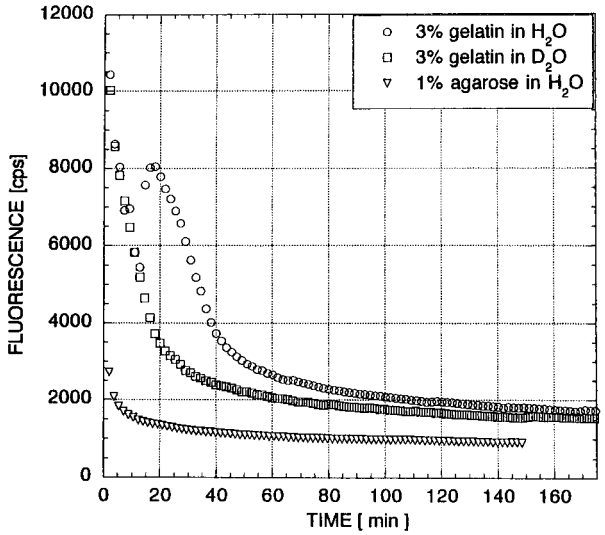


Fig. 3. Integral fluorescence intensity *versus* time of acquisition.

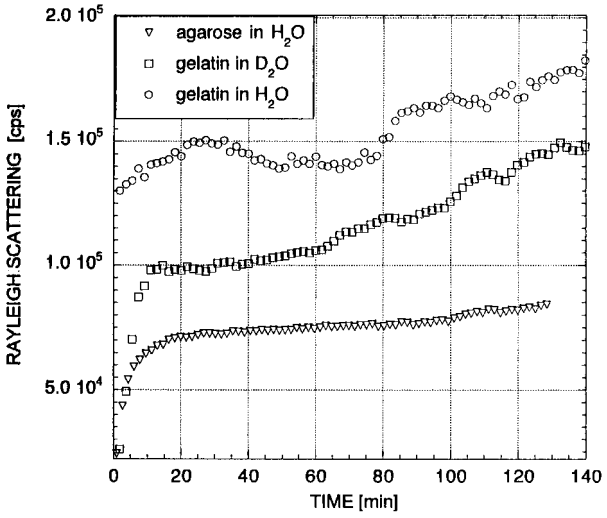


Fig. 4. Integral Rayleigh scattering intensity *versus* time of acquisition.

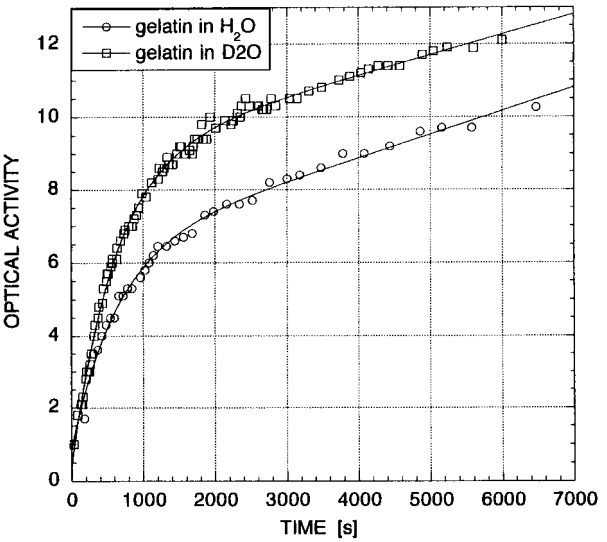


Fig. 5. Time evolution of helicity, obtained in optical activity measurements. Helicity is given in percents.

and normalizing them to the background intensity and the concentration of the solute. It can be seen that the fluorescence yield fall due to gel formation [7] is much more rapid in the agarose gel than in the gelatin gel. Besides that the gelatin dissolved in D_2O creates much stronger gel than the gelatin dissolved in H_2O. Waving of the curve corresponding to the H_2O gelatin solution is connected with the density fluctuations observed in vicinity of the sol-gel transition. We do not detect such fluctuations in the other two solutions because they organize themselves much more rapidly.

The plots in Figure 4 present, in turn, the time dependence of the integral scattered light intensity. The integral Rayleigh intensities have been calculated for spectra in Figures 2d–f by integrating the areas under the curves in the frequency range from 0 cm^{-1} to 50 cm^{-1} and normalizing them to the background intensity and the concentration of the solute. We can see that the intensity increases rapidly at the beginning of the process, then reaches certain constant value around which it starts fluctuating for some time. We will show below that this plateau value corresponds to the sol-gel transition. This stage of the intensity time evolution resembles the results of light scattering study of the gelation in the polymeric PMMA gels [8]. Anyway the results start to diverge in the next step of evolution. In the gels investigated by us the scattered light intensity starts rising up after certain time, when the gel is already formed. In the case of the PMMA gels the level of intensity remains constant.

Simultaneously with the fluorescence and scattering measurements we have performed the detection of the evolution of the optical activity of the medium. Unfortunately we were not able to make the observations in the aqueous agarose solution because it quickly becomes untransparent at the sol-gel transition. The results obtained for the H_2O and in D_2O gelatin solutions are shown in Figure 5. The angle of the rotation of the optical polarization is connected with the helicity of the medium by the formula [16]:

$$\frac{\chi}{\chi_{\max}} = \frac{\alpha_{\mathrm{m}} - \alpha_{\mathrm{coil}}}{\alpha_{\mathrm{collagen}} - \alpha_{\mathrm{coil}}} \cdot \qquad (1)$$

The helicity is defined as the ratio of the present number of intermolecular hydrogen bonds to the possible maximal number of bonds.

Theory

During gelation both the gelatin and agarose molecules try to construct the helical structure, thus linking together with hydrogen bonds at certain short sections of the long coils. We explain the phenomenon of the fluorescence quenching as due to formation of the network of the polymer molecules. In the sol state they group in separate

clusters, which then join together in one big cluster in the gel state [7,11]. In the language of the percolation theory we describe the size of the molecular cluster by the number of bonds, s, created between monomers within it and we denote by n_s the number of s-clusters per bond [1,7]. The intermolecular bonds are created with probability p. According to the definition of probability, p corresponds to the experimentally measured variable, the helicity χ. The probability P_s, that the molecule is conjugated to the finite cluster of s bonds is [1,3]:

$$P_s = sn_s \tag{2}$$

where n_s is defined as [1]: $n_s = (b_s/s)p^s(1-p)^{f+(f-2)s}$ and b_s is the total number of possible configurations of monomers creating s clusters, whereas f is the number of nearest neighbours of each monomer in a cluster. Thus, in the sol state:

$$P_s = \sum_s sn_s = p.$$

Above the gel point, at $p = p_c$, besides the many finite clusters we have also an "infinite" cluster with the maximal number of bonds $s_{\max}$. The probability $R(p)$ that the molecule belongs to this cluster, so called gel fraction, plays the role of the order parameter in the sol-gel transition. It is defined as:

$$R(p) \propto \begin{matrix} 0 & \text{in sol state} \\ (p-p_c)^\beta & \text{in gel state} \end{matrix}, \tag{3}$$

where β is the universal critical exponent, and $\sum_s sn_s + R(p) = p$ [1,3].

Fluorescence

Our assumption is that part of the excitation energy of the molecules, embedded in clusters, is dissipated in non-radiative process into the manifold of vibrational states of the cluster. We have shown in our previous work that the rate of the non-radiative transition $k^s_{\rm NR}$ depends on the number of intermolecular hydrogen bonds within the cluster [11]. It should increase with the cluster size. Applying the percolation theory we have found the relative fluorescence yield. It can be described by the following expression [7]:
a) in the sol state

$$\frac{I}{I_0} = c\left[1 - \sum_{s=1}^{M} P_s \frac{k^s_{\rm NR}}{k_{\rm R} + k^s_{\rm NR}}\right] \tag{4a}$$

b) in the gel state,

$$\frac{I}{I_0} = c\left[1 - R(p)\frac{k^\infty_{\rm NR}}{k_{\rm R} + k^\infty_{\rm NR}} - \sum_{s=1}^{M} P_s \frac{k^s_{\rm NR}}{k_{\rm R} + k^s_{\rm NR}}\right] \tag{4b}$$

where I_0 is the input light intensity, c is the gelatin concentration, $k^s_{\rm NR}$ is the nonradiative transition rate of such a cluster and $k_{\rm R}$ is the radiative decay rate. In the vicinity of the gel point, where the infinite cluster is being created, equations (4) yield [7,11]:

$$\left(\frac{I}{I_0}\right)_{S\to\infty} \to c\left[1 - \frac{k^\infty_{\rm NR}}{k_{\rm R} + k^\infty_{\rm NR}} \sum_{s=1}^{M\to M_{\max}} P_S\right] = c\left[1 - \frac{k^\infty_{\rm NR}}{k_{\rm R} + k^\infty_{\rm NR}} p\right], \tag{5}$$

which means that the fluorescence intensity follows the time dependence of the number of intermolecular bonds p. We assume that the gel point can be found in the middle of the region of the linear dependence $I(p)$. Above the gel point the fluorescence yield is given by the following power law:

$$\left(\frac{I}{I_0}\right)_{S\to\infty} \to c\left[1 - \frac{k^\infty_{\rm NR}}{k_{\rm R} + k^\infty_{\rm NR}}(p - p_c)^\beta\right]. \tag{6}$$

Our aim is to establish whether the critical exponent β depends on the type of the bonds linking molecules in the clusters.

Rayleigh scattering

According to the theory of elastic light scattering [19], the scattered light intensity per unite volume and at the distance r, corresponding to the wave vector $q = (4\pi n/\lambda)\sin(\theta/2)$ (θ is a scattering angle, λ is the incident light wavelength and n is the refractive index of the medium), has the form

$$I_R = BcM_{\rm W}S(q) \tag{7}$$

where $B = \frac{(4\pi)^4 I_0}{(\lambda n)^4 r^2}(\mathbf{n}_{\rm i} \cdot \mathbf{n}_{\rm s})^2$, c is the mass density of macromolecules, $\mathbf{n}_{\rm i}$ and $\mathbf{n}_{\rm s}$ are the polarization directions of the incident and scattered waves respectively, $M_{\rm W}$ is the weight averaged molecular weight and $S(q)$ is the z-average structure factor. In the solution of the polydisperse fractal aggregates it has the following limiting behaviour [8,9,19]:

$$S(q) = \left[1 + \frac{1}{3}(qR_{qz})^2\right]^{-1} \qquad R_{qz} < \frac{1}{q} \tag{8a}$$

$$S(q) = a(qR_{qz})^{-d^*_{\rm f}} \qquad R_{qz} \gg \frac{1}{q} \tag{8b}$$

where a is a constant, R_{qz} is the z-averaged radius of gyration, which describes the mean size of molecular aggregates, and $d^*_{\rm f} = d_{\rm f}(3-\tau)$ is the so-called effective fractal dimension of the system, $d_{\rm f}$ is the fractal dimension, τ is the universal polydispersity exponent. In our case $\lambda = 532$ nm, $n = 1.5$, $\theta = 90°$, thus $q = 3.9 \times 10^5$ cm^{-1}.
Percolation theory describes well the behaviour of the system in the sol state. Then, $M_{\rm W}$ and R_{qz} correspond to the average molecular weight and radius of gyration

of the finite clusters and are defined as [3,4]:

$$M_{\mathrm{W}} = \sum_s sP_s \xrightarrow[p\to p_{\mathrm{c}}]{s\to\infty} \left|p_{\mathrm{c}} - p\right|^{-\gamma} \qquad \text{for } p < p_{\mathrm{c}} \qquad (9)$$

and

$$R^2_{qz} = \frac{\sum\limits_s r^2 sP_s}{\sum\limits_s sP_s} \xrightarrow[p\to p_{\mathrm{c}}]{s\to\infty} \left|p_{\mathrm{c}} - p\right|^{-2\nu} \qquad \text{for } p < p_{\mathrm{c}} \qquad (10)$$

where summation goes over the finite clusters.

In view of the scaling law $\frac{\gamma}{2\nu} = \frac{1}{2}(3-\tau)d_{\mathrm{f}} = \frac{1}{2}d^*_{\mathrm{f}}$ we get the following relation in the sol state, in vicinity of the gel point [8,9]:

$$M_{\mathrm{W}} = b(R_{qz})^{d^*_{\mathrm{f}}}. \qquad (11)$$

At the beginning of the gelation process, in the sol state, the molecular aggregates are small what involves almost constant $S(q)$, as given by equation (8a). Thus, the Rayleigh intensity grows rapidly in time with the growth of the average cluster mass M_{W} [17], which is proportional to R^2_{qz} in dilute systems [18]. When the system is approaching the gel point $S(q)$ is given by equation (8b), M_{W}, by equation (11) and the scattered intensity saturates at certain value. Anyway in the gel state, where the "infinite" cluster appears equation (11) seems to be not valid. It has been shown [2] that in the system of large aggregates the radius of gyration increases slower that the average molecular mass due to size-dependent ring formation and lowering of the double bond reactivity. In such a situation equations (7) and (8) yield the increase of the scattered light intensity, which is in fact observed by us experimentally (see Fig. 4).

Herewith we try to expand the percolation approach on the gel state. Thus, in the gel state the weight averaged molecular mass M_{W}, and the radius of gyration R^2_{qz} include both finite clusters and an "infinite" cluster [3]:

$$M_{\mathrm{W}} = \sum_s sP_s + s_\infty R(p)$$
$$\cong (p-p_{\mathrm{c}})^{-\gamma} + (R^\infty_{qz})^{d_{\mathrm{f}}}(p-p_{\mathrm{c}})^{\beta} \quad \text{for } p > p_{\mathrm{c}} \qquad (12a)$$

$$\text{where} \quad R^\infty_{qz} \xrightarrow[s\to\infty]{} (s_\infty)^{\rho} = (s_\infty)^{1/d_{\mathrm{f}}} \quad \text{for} \quad p > p_{\mathrm{c}} \qquad (12b)$$

and s_∞ is the number of bonds in the "infinite" cluster.

Substituting equations (8b) and (12a) into equation (7) we get for $p > p_{\mathrm{c}}$:

$$I_{\mathrm{R}} \cong Bc(R^\infty_{qz})^{(d_{\mathrm{f}}-d^*_{\mathrm{f}})}(p-p_{\mathrm{c}})^{\beta}$$
$$= Bc(R^\infty_{qz})^{d_{\mathrm{f}}(\tau-2)}(p-p_{\mathrm{c}})^{\beta}. \qquad (13)$$

If we assume that $R^\infty_{qz} \approx (p-p_{\mathrm{c}})^{\alpha}$ we will get

$$I_{\mathrm{R}} \cong Bc(p-p_{\mathrm{c}})^{m}, \quad \text{where} \quad m = \beta + \alpha d_{\mathrm{f}}(\tau-2). \qquad (14)$$

Our aim is to find out experimentally whether the coefficient α is also a universal exponent. The percolation theory involves [3] $\beta = 0.45$, $\tau = 2.2$, $d_{\mathrm{f}} = 2.5$, thus it would give $m = 0.45 + 0.5\alpha$.

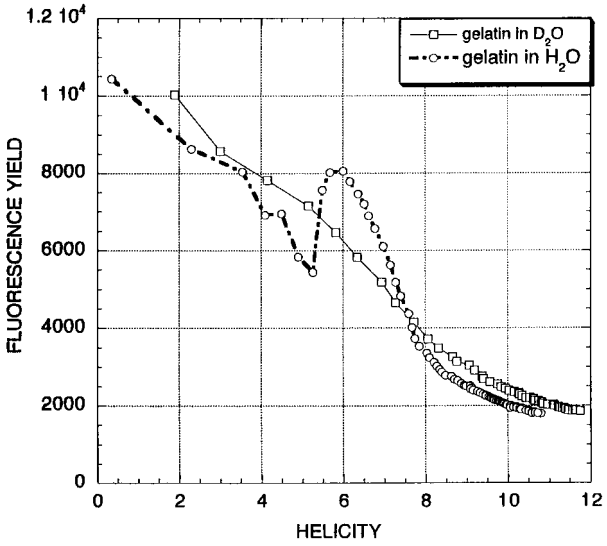


Fig. 6. Integral fluorescence intensity *versus* helicity. Helicity is given in percents.

Results and discussion

In order to obtain experimentally the dependence $I(\chi)$ of the fluorescence yield on the helicity of the medium we have eliminated time from Figures 3 and 5. The result is shown in Figure 6 for gelatin in H_2O and D_2O solutions. We have estimated the critical value of the helicity, χ_{c}, as lying in the middle of the region of the linear dependence $I(\chi)$ [11] and we have fitted the curve $I(\chi)$ for $\chi > \chi_{\mathrm{c}}$ to the power law given by equation (6). In order to obtain the critical exponents β for both solutions we have plotted the $(1-\frac{I}{I_0})$ as a function of $(\chi-\chi_{\mathrm{c}})$ on double logarithmic scale (see Fig. 7). The exponent β is established as a slope of the plot in the region where it becomes linear. The values of χ_{c} and of parameters β are presented in Table 1. It can be seen that the values of χ_{c} are slightly different in both studied solutions and the exponents β are almost the same within the experimental error. The discrepancies may be caused by inaccurate choice of the parameter χ_{c} [2,3]. Our result is in agreement with the values of β obtained by other authors [3] for gelation process. Moreover, comparison of the exponent β estimated by us with the one resulting from percolation theory (see Tab. 1) implies that the gelatin sol-gel transition, independently on the solvent considered, belongs to the same universality class as the random percolation on lattices [3]. The gel times for both solutions have been estimated from Figure 5 as the time corresponding to the χ_{c} values.

The dependence of the Rayleigh scattering intensity on the helicity of the medium, $I_{\mathrm{R}}(\chi)$, has been obtained by elimination of time from Figures 4 and 5. The resulting Figure 8 presents the plots $I_{\mathrm{R}}(\chi)$ for gelatin in H_2O and D_2O solutions. The plateau of the curves corresponds to the sol-gel transition. The gel point χ_{c}, found by us in the way described above, lies at the beginning of the plateau. In the gel state, above certain value of χ, the curves start rising up rapidly. To this part of the curve we have fitted

Table 1. The critical values and critical exponents obtained by numerical fits to experimental results.

material	χ_c	β	m	p	mp	Gel time
Gelatin in H_2O	7.5	0.45±0.01	3.28±0.01	0.14±0.01	0.46	35 min
Gelatin in D_2O	7.2	0.48±0.01	3.53±0.01	0.13±0.01	0.46	14 min
Agarose in H_2O	-	0.46*	3.3*	0.14±0.01	0.46*	20 min
Percolation theory		0.45 [3]				

* The value of m for agarose was taken the same as for gelatin, basing on the assumption that m is a combination of universal constants.

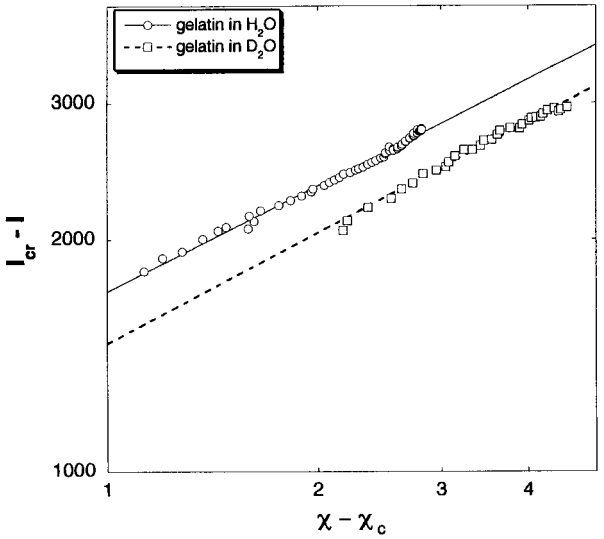


Fig. 7. The difference fluorescence intensity *versus* the difference of the helicity on the double logarithmic scale. $I_{cr} = I(\chi_c)$. The solid lines correspond to numerical fits to equation $(I_{cr} - I) = (\chi - \chi_c)^{\beta}$, where β is given in Table 1.

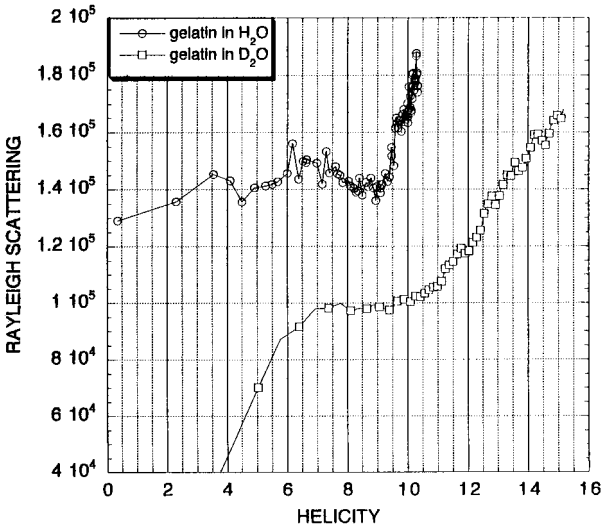


Fig. 8. Integral Rayleigh scattering intensity *versus* helicity. Helicity is given in percents.

the power law given by equation (14). The exponent m, defined in equation (14), is established as a slope of the plot of $(I_R - I_{Rcr})$ *versus* $(\chi - \chi_c)$ on a double logarithmic scale (see Fig. 9). I_{Rcr} is the plateau value. Since the plateau value corresponds to certain range of χ values, the result depends sensitively on the choice of the part of the fitted curve. Thus, for the curve $I_R(\chi)$ we have established the same range of χ as taken for the fit of the $I(\chi)$ curve. The estimated parameters m, shown in Table 1, appear to be the same for both solutions considered. We conclude that m is a universal exponent.

The exponent β for agarose gel has been found in another way. We have combined Figures 3 and 4 to obtain the dependence of the fluorescence yield on the Rayleigh scattering intensity, $I(I_R - I_{Rcr})$, for all three studied gels, which is shown in Figure 10. Than we fit part of the plot corresponding to the gel state, $I_R > I_{Rcr}$ by the power curve (see Fig. 11):

$$I = I_{cr} - (I_R - I_{Rcr})^p. \qquad (15)$$

Substituting the relation $I_R - I_{Rcr} \cong (\chi - \chi_c)^m$ into equation (15) we get the dependence $I(\chi)$ defined by equation (14) with $\beta = mp$. Thus, having found the exponent p and provided that m is the universal constant we can establish the exponent β for the agarose gel. Since in the case of the gelatin gels we have measured all three exponents we might check the validity of our assumption. The results are shown in Table 1. The gel time for agarose has been estimated from Figure 4 as the time corresponding to the beginning of the plateau of the Rayleigh intensity. It is longer than for D_2O gelatin solution, because we have studied the agarose solution

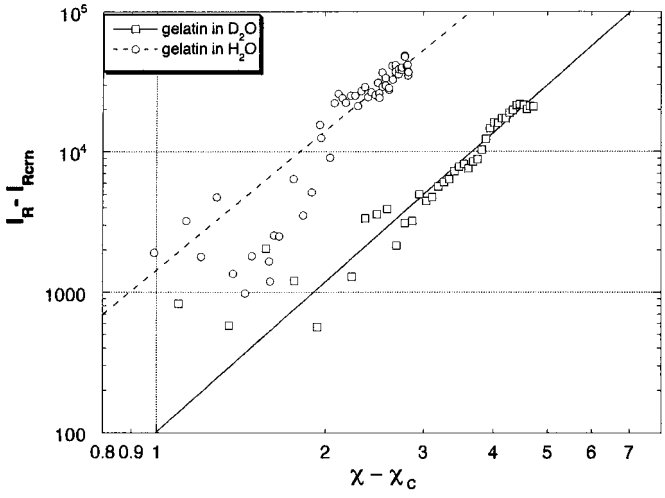
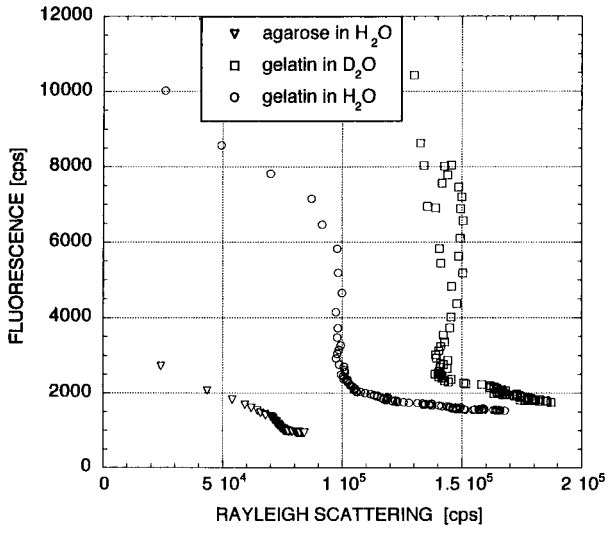
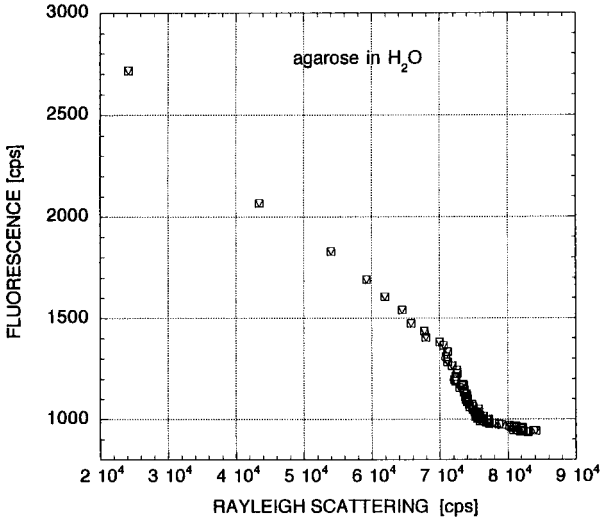


Fig. 9. The difference Rayleigh intensity *versus* the difference of the helicity on the double logarithmic scale. $I_{Rcr} = I_R(\chi_c)$. The solid lines correspond to numerical fits to equation $(I_R - I_{Rcr}) = (\chi - \chi_c)^m$, where m is given in Table 1.



(a)



(b)

Fig. 10. Integral fluorescence intensity *versus* integral Rayleigh scattering intensity; (a) all three materials, (b) enlarged agarose plot

of three times lower concentration. Gel time corresponds to the critical value χ_c, which is not a universal value.

The main conclusion from our study is that the gelation process of all physical gels considered belongs to the same universal class of processes, which can be well described by percolation theory and which are run by the same power laws.

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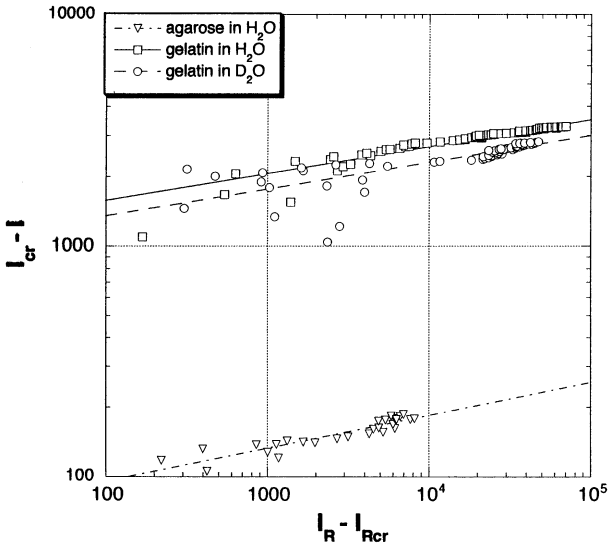

Fig. 11. The difference fluorescence intensity *versus* the difference of the Rayleigh scattering intensity on the double logarithmic scale. The solid lines correspond to numerical fits to equation $(I_{cr} - I) = (I_R - I_{Rcr})^p$, where p is given in Table 1.

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