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Universal critical exponents in the percolation approach to fluorescence and ultrasound studies of the gelation process

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Abstract

Here we present a sensitive spectroscopic method, which allows monitoring of the kinetics of creation of intermolecular bonds during the gelation process. We report the time evolution of the fluorescence spectra and the ultrasound velocity observed in two gelling materials with different kinds of intermolecular bonds, tetramethoxysilane solution and aqueous gelatin solution, during the sol–gel transition. Our results provide experimental evidence of a universal power law, resulting from the percolation theory, which connects the fluorescence yield and the ultrasound velocity. The values of the universal critical exponent a present in this law, found by us experimentally for all materials investigated, appear to be close to the value $a = 0.625$ predicted by percolation theory.

1. Introduction

Gels are very interesting materials to investigate as examples of self-organizing systems. The problem of whether the sol–gel transitions in different kinds of gels follow the same universal power laws attracts many scientists. In our previous studies [1–3] we have concentrated on reversible physical gels of gelatin and agarose. The gelation has been monitored by means of fluorescence and Rayleigh scattering measurements. We have found power laws and critical exponents describing this process. We have shown that the evolution of the stationary fluorescence yield of the dyes, embedded in the networks of gelatin molecules, reflects the kinetics of the intermolecular bond formation during the sol–gel transition. Both gelatin and agarose are organic biopolymers, wherein each polymer chain consists of about 1000 monomers [4] and the gel network is created due to hydrogen bonds between monomers of different chains. Here we investigate a gel with an entirely different type of bonding, the silica hydrogel [5], in which polymerization occurs by formation of chemical irreversible siloxane

bonds. Our aim is to compare the kinetics of the gelation process in the two kinds of gels and to find the universal power laws describing them.

In our measurements the gel formation is monitored by two methods performed simultaneously. The first one is the study of the time evolution of the fluorescence yield of the dye or another luminescent material diluted in the gelling solution and the second one depends on recording the time evolution of the velocity of the weak ultrasound wave passing through the sample. The first method has been used by us in our gelatin studies [1–3]. It has also been applied to silica gels for investigation of the drying process [6]. The measurements have been performed on the silica gel for two pH values and, for comparison, on the gelatin gel. We are interested in the sol–gel transition, particularly in establishing the gel time for the gels studied. The fluorescence yield of the luminescent materials appears to be very sensitive to the changes of the molecular surroundings. During gelation the fluorescence yield decreases and almost reaches a stable level in the gel state. We have proved that this phenomenon is connected with formation of a gel network. In the sol state the monomers instead group in separate clusters, which then join together in one big cluster in the gel state. We define the gel time as the time at which the big cluster, filling the whole volume of the sample, appears. The rate of the nonradiative transition depends on the number of intermolecular bonds within the cluster. It should increase with the cluster size. The velocity of the ultrasound wave also reflects such a phenomenon in all gels investigated. It decreases in the process of gelation in the same way as in a liquid with growing density, which confirms that there is molecular cluster formation in the gelation process [7]. Elimination of time from the two measurements allows us to find the dependence of the fluorescence yield on the sound velocity. We have described this dependence in terms of percolation theory and thus we have formulated the appropriate power law, which is obeyed in the vicinity of the gel point. Numerically fitting the theoretical curve to the experimental results enables us to find the corresponding critical exponent. Moreover, we have established the gel times for the gels studied as the times corresponding to the critical values of the fluorescence yield and ultrasound velocity at the gel point.

2. Experimental details

The scheme of the experimental set-up was the same as in our previous papers [1]. As the light source we used a 100 mW power Ar ion laser at 488 nm wavelength. We made our silica gels from tetramethoxysilane (TMOS) water solution using a two-step process [5]. The TMOS was first hydrolysed by dissolving it in dilute HCl (pH = 2) and stirring. Then we added an acetic buffer to raise the pH of the final solution to the range $4.5 < \text{pH} < 6$. In this range the solution starts to gel, whereas the gel time decreases for higher pH values [8]. The solution obtained is transparent and thus appropriate for optical measurements. It does not exhibit its own fluorescence in the range of visible frequencies. In order to monitor the structural changes in the gel studied we have monitored the fluorescence yield of two luminescent materials, which show strong absorption in the range of the incident laser light:

- (i) the diluted fluorescein dye added to the solution at low concentration $c = 0.001 \text{ mg}/100 \text{ cm}^3$ and
- (ii) the salt of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (uranile nitrate) at the concentration $c = 0.005\%$.

The gelatin sample, from pig skin, bloom test 150, was provided by British Drug House Ltd, Poole, UK.

The measurements for silica gel were made at two pH values, 4.8 and 5.6, at the temperature $T = 22^\circ\text{C}$, and for pH = 5.6 also at the temperature $T = 25^\circ\text{C}$. The measurements for gelatin gel were performed at the temperature $T = 22^\circ\text{C}$. The stabilization of the temperature was

ensured by use of a jacketed cell. The fluorescence spectra, resolved by a 0.5 m monochromator, were acquired every 90 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 second experimental method, synchronized in time with the fluorescence yield detection, depended on measurements of the velocity of the ultrasound wave passing through the sample. The ultrasound experiment was performed in a thermally stabilized cell. The intensity of the sound wave had to be very low in order to avoid ultrasound induced polymerization phenomena [8]. The time intervals between the successive acquisitions in the two experiments have been established to be the same, so the time variable could be eliminated and the direct dependence of the fluorescence yield on the ultrasound velocity was obtained.

3. Theoretical

The velocity of sound propagating in a liquid is given by the equation [9]

$$v = \frac{1}{\sqrt{\rho\beta_S}} \tag{1}$$

where ρ , β_S denote the density and the compressibility of a liquid, respectively.

In the gel state, for $p > p_c$, in the region where the dimension L of the infinite ‘cluster’ is much larger than the characteristic correlation length ξ [10] (whereas $\xi \propto |p - p_c|^{-\nu}$ in the vicinity of the gel point), the sound velocity scales according to the formula [11, 12]

$$v \propto \xi^{-\frac{\theta}{2}} \propto (p - p_c)^{\frac{\theta}{2}} \quad p > p_c \tag{2}$$

with critical exponents ν and θ . θ is the dynamical index related to the scaling phenomena of the elastic constant, the conductivity and the diffusion constant. Substituting the scaling power laws for the density and compressibility of the infinite cluster [10]

$$\begin{aligned} \rho_\infty &\propto \xi^{-\frac{\beta}{\nu}} \propto (p - p_c)^\beta \\ \beta_{S\infty} &= \frac{1}{E} \propto (p - p_c)^{-t} \end{aligned} \tag{3}$$

into equation (1) and comparing the outcome with equation (2), we get $\theta = (t - \beta)/\nu$.

In the sol state, the appropriate formula for the sound velocity can be obtained by use of the scaling approach [11–13]:

$$v \propto L^{-\frac{\theta}{2}} f\left(\frac{L}{\xi}\right) \quad p < p_c \tag{4}$$

where $f\left(\frac{L}{\xi}\right)$ is the scaling function:

$$\begin{aligned} f\left(\frac{L}{\xi}\right) &\xrightarrow{L \gg \xi} \left(\frac{L}{\xi}\right)^{\frac{\theta}{2}} \\ f\left(\frac{L}{\xi}\right) &\xrightarrow{L \ll \xi} 1. \end{aligned} \tag{4a}$$

Equation (4) implies $v \propto L^{-\frac{\theta}{2}}$ for the sol state with small clusters. When approaching the gel point, equation (4) takes the form

$$v \propto L^{-\frac{\theta}{2}} f(L^{\frac{1}{\nu}}|p - p_c|) \quad L \rightarrow \infty, \quad p \rightarrow p_c. \tag{5}$$

The crossover region occurs for $L = \xi$, which occurs at the gel point for $p = p_c$, since the two variables approach the gel point according to the same power law [10]: $L \propto |p - p_c|^{-\nu}$ and $\xi \propto |p - p_c|^{-\nu}$. The critical value of the ultrasound velocity $v_c = v(p_c)$ can be obtained as the crossing point of the curves given by equations (2) and (4), extrapolated to the region for $L = \xi$. Anyway, in the finite cavity the dimension L becomes the dimension of the sample and we do not observe the region $L \gg \xi$. Thus, in the gel state we expect a constant value of the ultrasound velocity:

$$v = v_c \quad p \geq p_c. \quad (6)$$

Assuming that the scaling function $f(L^{\frac{1}{\nu}}(p - p_c)) = 1$ for $p = p_c$, we get the behaviour of the ultrasound velocity on the sol side in the form

$$v - v_c \propto (p - p_c)^{\frac{\nu\beta}{2}} \quad p < p_c. \quad (7)$$

Our aim is to find the dependence of the ultrasound velocity on the fluorescence yield. In our previous papers [3] we have found the dependence of the dye fluorescence yield I on the fraction of the intermolecular bonds p being created within the gel network during the gelation process. In the vicinity of the gel point, when approached from the sol side, it takes the form

$$I(p) \rightarrow I_c[1 - A(p - p_c)], \quad (8)$$

where $A = \frac{\alpha}{1 - \alpha p_c}$ and $\alpha = \frac{k_{NR}^{\infty}}{k_R + k_{NR}^{\infty}}$ denotes the ratio of the rate of the nonradiative transitions to the sum of those of the radiative and nonradiative transitions responsible for the fluorescence quenching; p_c and I_c denote the critical values of the bond fraction and the fluorescence yield at the gel point, respectively; I_0 is the initial value of the fluorescence yield. The gel point has been assumed to be found [1, 3] in the middle of the region given by equation (8). Substituting $(p - p_c)$, derived from equation (8), into equation (7) we get the ultrasound velocity as a function of the fluorescence yield:

$$\begin{aligned} v - v_c &\propto \left(\frac{I - I_c}{AI_c}\right)^a && \text{for } p < p_c, \text{ which means } I > I_c \\ v &= v_c && \text{for } p > p_c, \text{ which means } I < I_c \end{aligned} \quad (9)$$

where $a = \frac{t-\beta}{2}$. In percolation theory, $t = 1.7$, $\beta = 0.45$, which implies that $a = 0.625$.

4. Results

The results of our fluorescence studies of silica gel are presented in figures 1 and 2. Figure 1 shows an example of a sequence of fluorescence spectra of the fluorescein (figure 1(a)) and the uranile nitrate (figure 1(b)) dyes diluted in TMOS water solution of pH = 5.6, taken every 90 s during the gelation process at the temperature $T = 22$ °C. The concentration of the dyes has been made very low in order to avoid mutual secondary excitation of the dye molecules. The time dependence of the fluorescence yield is illustrated in figure 2, in which, on the vertical axis, we have plotted the values of the integrals over the area of the fluorescence peak in the spectra as in figure 1, normalized to the input laser intensity. Figures 2(a), (b) contain plots drawn for fluorescein and uranile nitrate, respectively, diluted in TMOS solutions at two values pH = 5.6 and 4.8. In figure 2(a) there are separate vertical axes for the two pH values, since the absorption efficiency of fluorescein at pH = 4.8 is much lower than that at pH = 5.6 [14]. In order to show the temperature effect the measurements for the fluorescein in the pH = 5.6 solution were performed also at the temperature $T = 2$ °C; the results are shown in figure 2(a). It can be seen that the fluorescence yield in the gel state tends to a lower value at higher temperature, which is opposite to the result observed for gelatin gels [1]. This

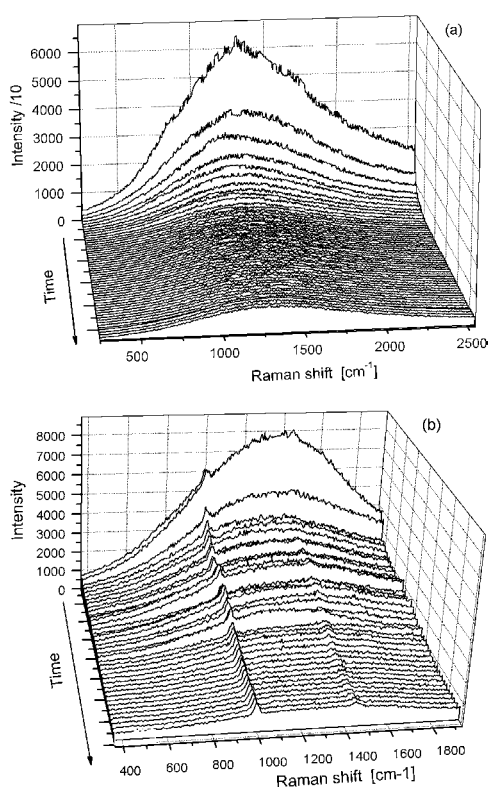


Figure 1. The time evolution of the fluorescence spectra of: (a) the fluorescein dye and (b) the uranile nitrate dye, diluted in the TMOS solution.

suggests that the fraction of the dye energy lost to nonradiative processes [1, 3] in silica gel is bigger at higher temperature, which, in turn, implies that the number of intermolecular bonds is higher. Our conclusions are in agreement with the results of other authors [8, 15, 16]. It is a known fact [8, 15, 16] that in silica gels the temperature helps the densification of the material, whereas in biopolymer gels the temperature spoils the hydrogen intermolecular bonds. For comparison, in figure 2(c) we present the time dependence of the fluorescence yield of the fluorescein diluted at the same concentration in the 5% aqueous gelatin solution. We can see in figure 2 that the evolutions of the fluorescence yield have similar character independently of the gel type. It rapidly decreases in the sol state and slowly tends to a certain constant value in the gel state. For silica gel the rapid decrease is pH dependent, which proves that the time of gelation is pH dependent. The process of gelation is much slower for smaller pH values (see figures 2(a), (b)). This is well known from all silica gel studies [8]. We should stress also that, due to the low absorption efficiency of fluorescein [14], the dynamics of the process in the solution of pH = 4.8 occurs much more slowly than that in the solution of pH = 5.6. In the latter case the fluorescence yield is quenched by almost a factor of three, whereas in the former case it is only by a factor of 1.6. The fluorescence of the uranile nitrate is not pH sensitive in the region investigated. There is another feature that appears in the spectra of the uranile nitrate, of the fluorescein in gelatin and also of the fluorescein in TMOS for pH = 4.8. The fluorescence yield exhibits strong fluctuation upwards just before it approaches the gel state. We explain this phenomenon, which was observed by us previously [2], as due to density fluctuations near the sol–gel transition.

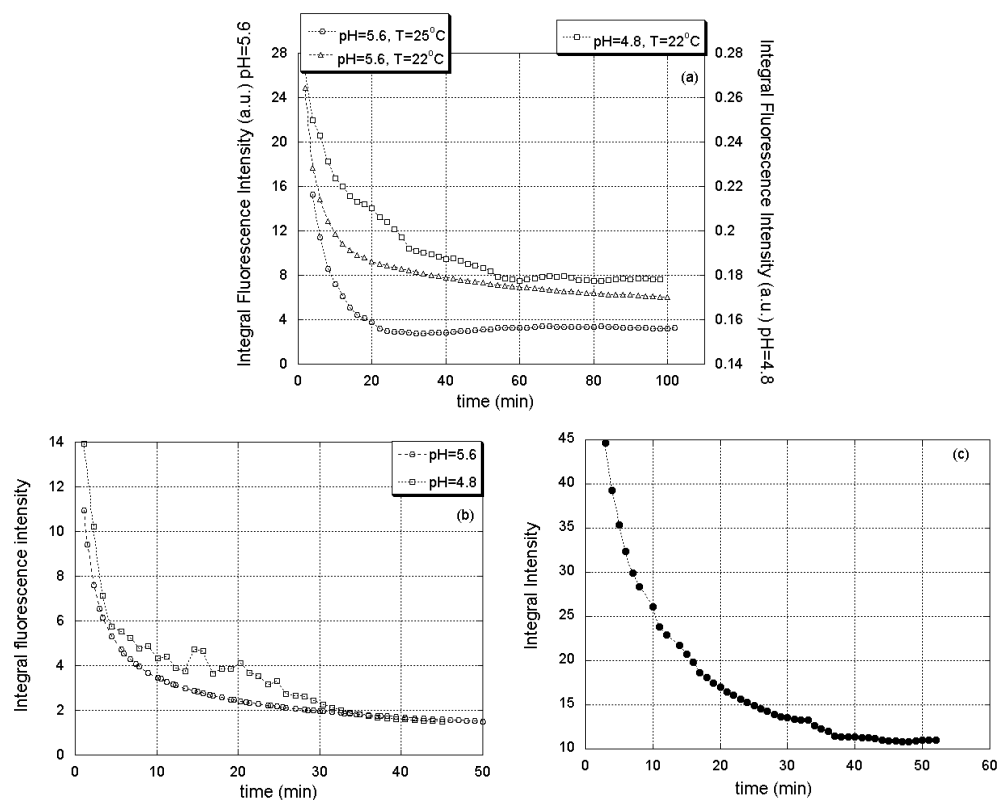


Figure 2. The integral fluorescence intensity, normalized by the intensity of the input laser beam, versus time of acquisition for: (a) fluoresein in TMOS solution; (b) uranile nitrate in TMOS solution; (c) fluoresein in 5% aqueous gelatin solution at the temperature $T = 22^\circ\text{C}$. The error bars are smaller than the markers of the experimental points.

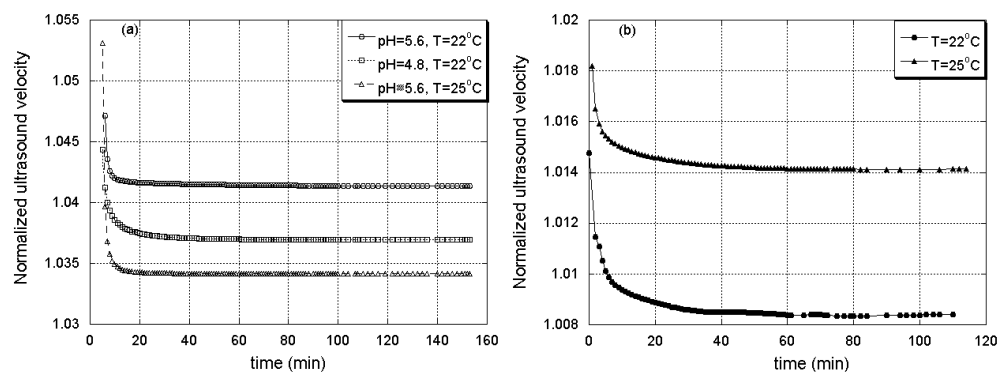


Figure 3. The time evolution of the ultrasound velocity in: (a) TMOS; (b) 5% aqueous gelatin solution. The error bars are smaller than the markers of the experimental points.

The results of the ultrasound velocity measurements are shown in figure 3, both for TMOS and for the gelatin solution. The values of the ultrasound velocities detected have been divided by the ultrasound velocity in bulk water. It can be seen that in all cases, in the sol state as well as in the gel state, the ultrasound wave propagates quicker than in water. According

Table 1. The critical component a , given by equation (9), the coordinates of the gel point extracted from figure 4 and the gel times found from figures 2 and 3.

	a	I_c	v_c	Gel time (min)
Gelatin	0.715	12.0	1.0085	35
TMOS pH = 5.6 $T = 22^\circ\text{C}$ (fluorescein)	0.681	10.4	1.0418	13
TMOS pH = 5.6 $T = 22^\circ\text{C}$ (uranile nitrate)	0.650	3.100	1.0418	13
TMOS pH = 5.6 $T = 25^\circ\text{C}$ (fluorescein)	0.583	5.880	1.034	12
TMOS pH = 4.8 $T = 22^\circ\text{C}$ (fluorescein)	0.637	0.187	1.0370	40
TMOS pH = 4.8 $T = 22^\circ\text{C}$ (uranile nitrate)	0.642	1.640	1.0370	40

to equation (3), we can conclude that the product of the density and the compressibility in the solutions investigated is smaller than that for water, which means that the increase of the density is much smaller than the decrease of the compressibility in the solutions, unlike the case for water. In the course of the gelation we observe rapid quenching of the ultrasound velocity to the almost stable value for the gel state, which is closer to that for bulk water but still bigger than it. We explain this phenomenon in the following way. When the network of the solute molecules is being created the density of the system increases due to the increase of the average molecular weight of the clusters [8]. The compressibility of the gels is smaller than that of bulk water, since water in gel pores partly loses its tetrahedral structure and this leads to denser packing [17]. In the gelatin gel the ultrasound velocity increases with temperature, due to the decrease of the density and also due to the decrease of the compressibility. Such behaviour of the ultrasound velocity is typical for water, which constitutes 95% of the gelatin solution. In the silica gel the situation is again opposite. The compressibility of the system increases with temperature [8]; thus the ultrasound propagates with smaller velocity at higher temperatures. The ultrasound velocity is established at a lower level when the concentration of hydrogen ions in the silica gel is higher, v_c (pH = 4.8) < v_c (pH = 5.6). In order to check the power laws proposed in section 3 and to obtain the dependence of the ultrasound velocity on the fluorescence yield $v(I)$ we have combined the results of figures 2 and 3 by eliminating time. The results are shown in figure 4 on a log–log scale. The fluorescence intensity passes from larger to smaller values as the gelation process proceeds. The linear parts of the plots, drawn on a log–log scale, have been fitted with straight lines. The gel point has been estimated as the crossing point of these lines. The critical exponent, a , present in the power law given in equation (9) is found as the inclination of the plot $\log(v - v_c) = a \log(I - I_c)$. The critical exponents a and the coordinates of the gel points (I_c, v_c) obtained in this way for all plots in figure 4 are presented in table 1. We can see that in all cases the values of the

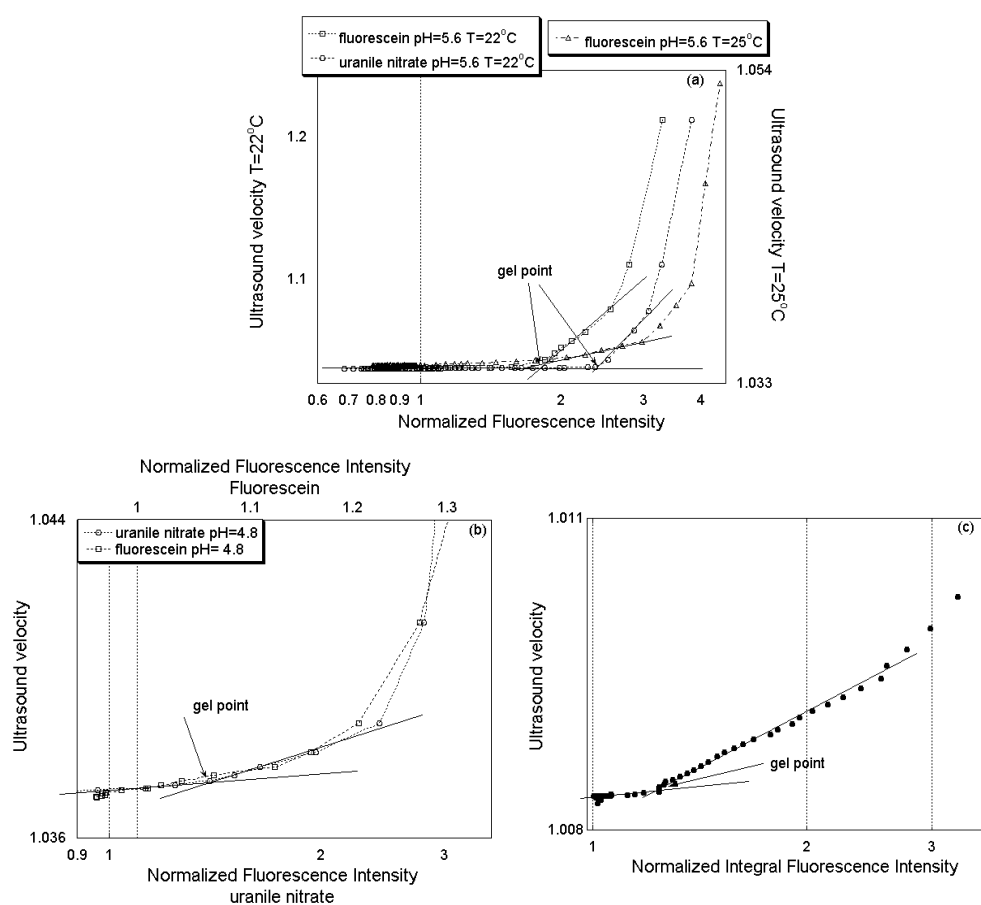


Figure 4. The log–log plot of the ultrasound velocity versus the integral fluorescence intensity. The fluorescence intensity has been normalized by the value I_s , corresponding to the lowest value in figure 2. The straight lines show the slopes of the curve near the gel point. (a) TMOS at pH = 5.6, $I_s = 6$ for fluorescein at $T = 22^\circ\text{C}$, $I_s = 3$ for fluorescein at $T = 25^\circ\text{C}$, $I_s = 1.5$ for uranile nitrate at $T = 22^\circ\text{C}$; (b) TMOS at pH = 4.8, $I_s = 0.18$ for fluorescein at $T = 22^\circ\text{C}$, $I_s = 1.55$ for uranile nitrate at $T = 22^\circ\text{C}$; (c) 5% aqueous gelatin solution at the temperature $T = 22^\circ\text{C}$, $I_s = 11$. The error bars are smaller than the markers of the experimental points.

critical exponent a found by us experimentally are close to the value $a = 0.625$ predicted by percolation theory. The discrepancies between the corresponding values shown in table 1 are caused by inaccuracy in choosing the gel point. The results presented in this paper prove that the two gels studied belong to the same class of universality, which can be described by percolation theory. Moreover, their behaviour does not depend on the pH value of the solution or on the temperature.

5. Summary and conclusions

We have presented two experimental methods of monitoring the gelation process, i.e. detection of the time evolution of the fluorescence yield of the dye embedded in the gel network and of the velocity of the ultrasound wave passing through the medium. Synchronization in time of

the two methods allows us to find the dependence of the ultrasound velocity on the fluorescence yield, which, on the other hand, has been described in terms of percolation theory by a universal power law. By numerically fitting the experimental plot with the theoretical curve we obtain the universal critical exponents present in this law. The measurements have been performed for two gels with different kinds of intermolecular bonds, the chemical silica gel and the physical gelatin gel. The two gels exhibit different physical features, which results in there being discrepancies as regards the dynamics of the gelation process. However, it appears that the values of the universal critical exponents are the same for the two gels, within experimental error, which means that they belong to the same universality class.

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