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Investigation of drying silica gel by fluorescence methods

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Abstract

Results of steady-state and time-resolved fluorescence studies for a model drying process of selected silane gels are discussed in the paper. Gels which contained a fluorescence probe in the form of pyrene, at pH 4.1 and 5.9 were dried in the oxygen-free atmosphere, using a vacuum system. After subsequent stages of the drying process the spectra of fluorescence excitation and emission as well as fluorescence decay curves were recorded using the time-resolution techniques. On this basis micropolarity of the environment of pyrene encapsulated in gel pores and changes in the excimer intensity of a probe during the process were determined.

A kinetic model of drying for the tested gels and the value of a drying rate constant were specified on the basis of the determination of the number of moles of water and ethanol evaporated from the gel. The analysis of lifetime distributions of particular pyrene forms led to the conclusions concerning changes in the fluorophore environment during the gel–xerogel transition connected with the evaporation of solvents from gel pores and next with a decrease of the pore sizes.
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Keywords: Gel–xerogel transition; Pyrene; Silane; Steady-state fluorescence; Time-resolved fluorescence

1. Introduction

Silane gel has become recently one of the most attractive inorganic carriers that are used successfully in the immobilisation of organic probes, including biologically important compounds such as enzymes, without damaging them [1–3]. Because of their properties such as transparency, mechanical stability, very good hardness and structure close to quartz, these gels have found application in optical studies for laser construction [4–8] and in biotechnology [9], in the construction of optical sensors used for the measurement of pH [10,11], oxygen [12], glucose [13], hydrogen peroxide [14] and ammonia [15]. The silane carrier formed using the sol–gel technique, is characterised by different porosity depending on the initial conditions of a starting sol, i.e. its composition and pH [16], type of catalyst used [17] and gelation temperature. It is known from the research carried out so far that a newly formed gel is subject to further structural changes in the process of ageing [18]. As a result of drying which consists in evaporation of solvent particles, i.e. water and alcohol from gel mass, also the carrier structure, its pore shape and size change [19,20]. The final form of xerogel is determined by gel drying conditions, i.e. process rate, gel storage conditions and drying atmosphere [21].

In this paper results of fluorescence studies on gel–xerogel transition using model drying, in oxygen-free atmosphere, with pyrene as a fluorescence probe are discussed. For experiments two gels were selected, which were formed as a result of acid hydrolysis from sol at pH 4.1 and 5.9. From literature and previous research [22] it followed that gels for pH values mentioned above, were characterised by different structure. After subsequent stages of each gel drying, fluorescence steady-state spectra for pyrene were recorded at $\lambda_{em} = 392$ nm (monomer) and $\lambda_{em} = 470$ nm (excimer). The fluorescence decay kinetics of the probe was also recorded after these stages. The measurement and analysis of fluorescence and time-resolved spectra were carried out to supply information on local changes in micropolarity in the neighbourhood of pyrene molecule during gel–xerogel transition. On this basis conclusions can be drawn on changes in the gel net structure formed as –Si–O–Si– which took place in the dynamic process of drying. It was also possible to determine the kinetics of model drying and compare drying process rates in these conditions.

2. Experimental

In the measurements the following compounds were used: pyrene (Aldrich) additionally purified by recrystallisation from ethanol, spectrally pure ethanol (P.O.

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Ch. Gliwice), hydrochloric acid (HCl) p.a. (P.O Ch. Gliwice), tetraethylorthosilicate (TEOS) (Aldrich) as well as distilled and deionised water. The starting sol consisted of TEOS:ethanol:water in molar ratio 1:6:6. A solution of pyrene in ethanol of concentration 4×10^{-4} M was used. The pH of sol was adjusted by adding properly diluted HCl. The gel was obtained from sol deaerated on the vacuum line, in the cell made from special optical glass (Hellma), closed with a stopcock. Samples were stored at 20 °C.

Drying of gels started 2 months after both samples had been gelated. Vapours of water and ethanol were removed in cycles using the vacuum line and recording time of measurements and pressure changes on a mercury manometer. Results were converted into the number of moles of solvent vapours assuming constant temperature of measurements equal to 20 °C.

Steady-state fluorescence spectra were recorded at $\lambda_{ex} =$ 337 nm, using the Fluoromax-2 apparatus, Jobin Yvon, while the emission of pyrene lifetimes in the time-correlated single photon counting system from Edinburgh Analytical Instruments.

3. Results and discussion

3.1. Steady-state emission spectra

Two silane gels, with different pH of the starting sol, which were subjected to drying, were obtained at the temperature 20 °C, in the oxygen-free atmosphere. The gel of pH 4.1 was formed after 6 days, while the one with pH 5.9 after 16 days. The gels were transparent and homogeneous. From previous fluorescence studies and literature survey it followed that the gels differed also in their structure [16,22]. On the basis of analysis of pyrene lifetime decay kinetics during gelation, it could be concluded that the gel of pH 4.1 was characterised by most probably larger pores than those of the carrier of pH 5.9. A domain of lifetime characteristic of an isolated pyrene molecule in the monomeric form was identified in it, with a long lifetime reaching 200 ns and a pyrene excimer (45 ns), while in the gel with higher pH there were only pyrene aggregates with short lifetimes of 50 ns and dozen nanoseconds, responsible for the excimer and dimer. The gels were left for a couple of months in unchanged conditions, in the oxygen-free atmosphere, until the gel network had been formed after the sol–gel transition.

After 2 months of storing the samples at the temperature 20 °C with no air access, i.e. in such conditions in which they were formed, the process of drying started. The vapours of water and ethanol mixture were removed in cycles using the vacuum line. After each cycle the steady-state fluorescence excitation and emission spectra and fluorescence decay kinetics of pyrene were recorded in the tested gels. Fig. 1 shows selected fluorescence emission spectra of pyrene in the gel of pH 4.1 after subsequent drying cycles. The last spectrum was recorded for a cracked gel destroyed as a result of impact of the vacuum line.

A similar experiment was carried out for the gel of pH 5.9. In both the cases an increase of the intensity of the probe fluorescence emission was observed during drying of the gel in the measured wavelength range. A maximum at 418 nm, ascribed by some authors to the presence of pyrene dimers [23] and a maximum at 467 nm, responsible for a dynamic excimer formation were also reported. Changes in the intensity ratio of bands 371, 381 and 467 nm were recorded. These results were closely related to the change of the

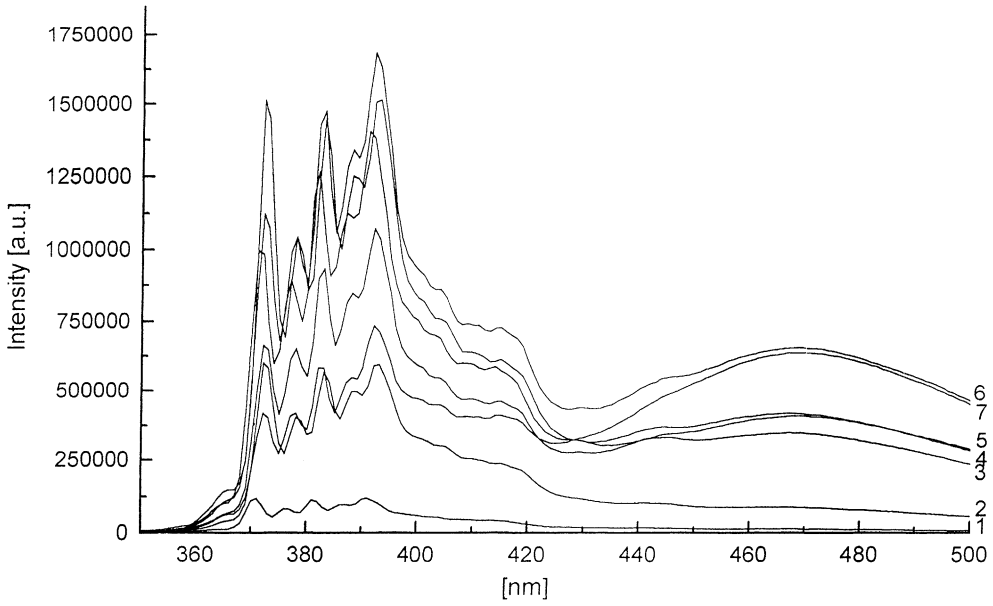

Fig. 1. Fluorescence spectra of pyrene in the gel–xerogel system at the consecutive steps of drying: n (mol) = (1) starting gel, (2) 0.0006, (3) 0.0023, (4) 0.0119, (5) 0.0363, (6) 0.04078, (7) 0.05120. Concentration of pyrene 4×10^{-4} M, pH 4.1, $\lambda_{ex} = 337$ nm.

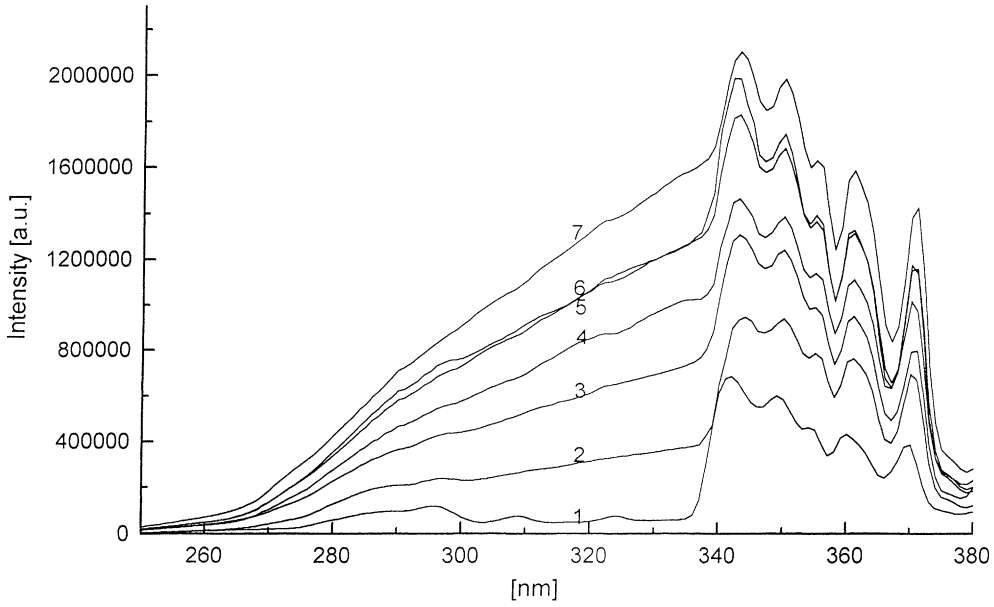

Fig. 2. Excitation spectra of pyrene in the gel–xerogel system at the consecutive steps of drying: n (mol) = (1) starting gel, (2) 0.0006, (3) 0.0023, (4) 0.0119, (5) 0.0363, (6) 0.04078, (7) 0.05120. Concentration of pyrene 4×10^{-4} M, pH 4.1, $\lambda_{em} = 392$ nm.

nearest surroundings of probe molecules during drying which was a consequence of the decreasing amount of water and ethanol in gel pores. Due to this the fluorescence of excited pyrene molecules was quenched to a lesser extent. Other researchers obtained similar results during drying of silane materials formed by the sol–gel method, containing pyranine or 7-azaindole [20]. An analogous tendency of changes in fluorescence intensity was reported for excitation spectra collected after subsequent stages of drying (Fig. 2). In this case an increase of fluorescence intensity during gel drying was closely linked with the decay of a subtle spectrum in the range 270–320 nm, which might confirm the presence of pyrene dimers [23].

Pyrene is used successfully as a fluorescence probe in research on systems in which polarity changes [21,24–26] because the ratio of the third (I_{381}) to first (I_{371}) peak in its subtle emission spectrum is the measure of micropolarity of the probe surroundings in the tested sample. On the basis of steady-state fluorescence emission spectra of pyrene, the value of I_{381}/I_{371} was determined for the tested gels as a function of the number of moles of evaporated solvent mixture (Fig. 3). For both the gels an increase of I_{381}/I_{371}

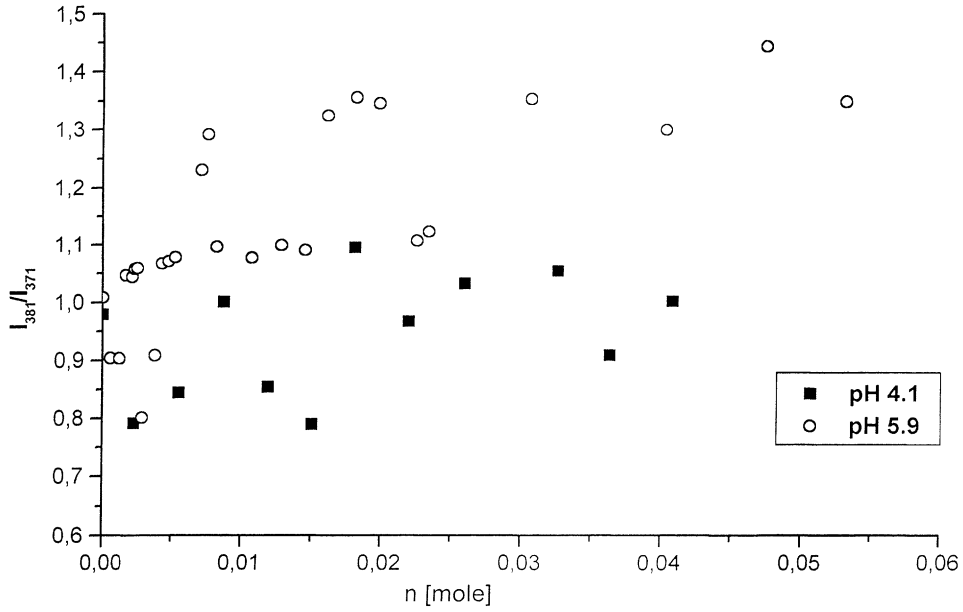

Fig. 3. Changes of polarity during drying of gels for various pH of starting sol: (■) pH 4.1, (○) pH 5.9.

was observed during drying, particularly in the first period, which denoted a decrease of polarity in the surroundings of pyrene molecules [21,24]. These results were explained by a removal of water and ethanol from gel pores in the closest surroundings of pyrene. The water and ethanol are known to be more polar than –Si–O–Si– groups that form the xerogel frame and silanol groups –Si–OH, built into the gel structure [27]. Higher values of this ratio were reported for the gel of pH 5.9. The final value of I_{381}/I_{371} obtained as a result of drying the sample at pH 4.1 corresponded to the polarity similar to that of xylene, while at pH 5.9 to the polarity of aliphatic hydrocarbons [28]. Differences observed in I_{381}/I_{371} were related to a different gel structure which depended on the pH of the starting gel [16]. Lower micropolarity in xerogel pores at pH 5.9 as compared to xerogel at pH 4.1 was most probably a result of a more colloidal structure of the gel, which might be connected with lower porosity of the carrier at pH 5.9 and smaller size of the formed pores. Hence, the closest surroundings of the probe molecules would consist of pyrene molecules [29]. In the case of the xerogel of pH 4.1 which is formed during cross-linking of linear polymer chains, interactions between larger gel pores of probe molecules with hydroxyl groups –Si–OH of the gel net, not used in the formation of bigger pores, are possible. Hence the I_{381}/I_{371} ratio being a measure of polarity assumed higher values. Some authors suggest that this result is determined mainly by water molecules which are released in the time of condensation and polymer cross-linking. They are adsorbed on the pore surface and can be removed from it only at elevated temperature [30,31].

On the basis of steady-state fluorescence spectra of pyrene recorded during drying, also the I_{467}/I_{371} ratio was determined. This ratio describes the emission intensity of an excimer band at $\lambda_{em} = 467$ nm (Fig. 4). While removing solvent vapours from the gel at pH 4.1 under reduced pressure, an increase of pyrene fluorescence intensity in this region of the spectrum was observed. In the gel of pH 5.9 after reaching a maximum, a certain decrease of I_{467}/I_{371} was observed. The increase of I_{467}/I_{371} in subsequent drying cycles was attributed to a local increase of pyrene concentration caused by the removal of water and ethanol molecules from the gel pores [19,21,24]. The growth of excimer fluorescence intensity resulted most probably also from a decrease of gel pore volume and a change of its size (reorganisation) during drying [28,30,32]. The decrease of I_{467}/I_{371} in the final stage of xerogel formation at pH 5.9 can be related to the isolation of part of pyrene molecules in the newly formed pores of the xerogel or occurrence of ground-state pyrene aggregates in dried polymer cells [33].

3.2. Lifetime measurements

After subsequent cycles of gel drying at pH 4.1 and 5.9, respectively, in the oxygen-free atmosphere, also the kinetics of pyrene fluorescence decay was recorded at $\lambda_{em} = 392$ and 467 nm, which corresponded to monomer and excimer emissions, respectively. Fig. 5a and b illustrates the pyrene fluorescence decay curves for consecutive drying cycles of gel at pH 4.1. The experimental data collected for both gels were best fitted using the triple exponential equations:

$$I_M(t) = A_1 \exp\left(-\frac{t}{\tau_{M1}}\right) + A_2 \exp\left(-\frac{t}{\tau_{M2}}\right),$$

$$I_E(t) = A_1' \exp\left(-\frac{t}{\tau_{E1}}\right) + A_2' \exp\left(-\frac{t}{\tau_{E2}}\right)$$

The results of fitting the experimental curves are given in Tables 1 and 2. In all fits the component $\tau_3 = 5$ ns was

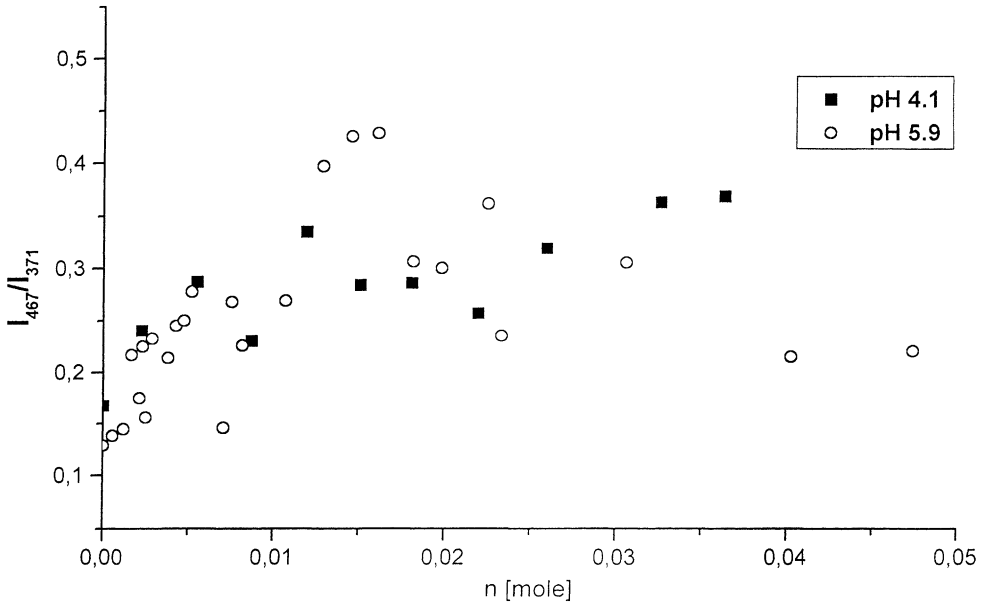

Fig. 4. Changes in relative excimer emission of pyrene during the gel–xerogel process: (■) pH 4.1, (○) pH 5.9.

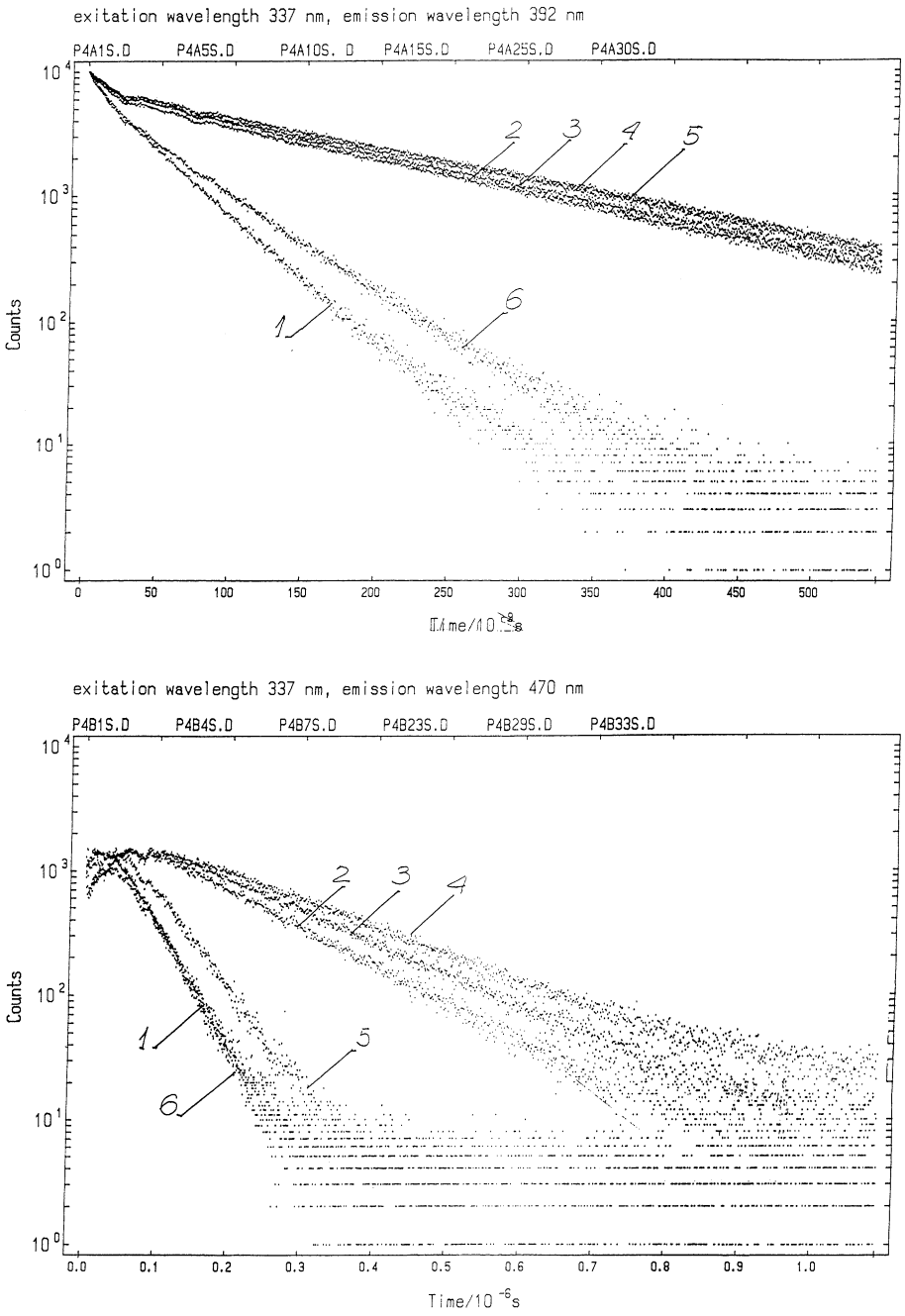

Fig. 5. Fluorescence decay curves of pyrene in the gel–xerogel system at the successive steps of drying: n (mol) = (1) 0.0006, (2) 0.0023, (3) 0.0049, (4) 0.0150, (5) 0.0474, (6) 0.0518. Concentration of pyrene 4×10^{-4} M, pH 4.1. (A) $\lambda_{em} = 392$ nm; (B) $\lambda_{em} = 470$ nm.

observed which was probably related to the fluorescence emission originating from an admixture present in the applied silane monomer. Therefore this result has not been given in Tables 1 and 2.

In the gel of pH 4.1 both at fluorescence decay at $\lambda_{em} = 392$ and 467 nm, prior to drying the lifetime was 50 ns. Taking into account the applied probe concentration 4×10^{-4} M, this result can be explained by the presence of pyrene excimer formed dynamically in the gel pores which is indicated by a negative pre-exponential factor [22]. The domain of time 80 ns ($\lambda_{em} = 467$ nm) originates probably from the isolated pyrene molecules present in gel pores in the neighbourhood of polar molecules of water and ethanol. Due to interactions with the surroundings, their lifetime was nearly three times shorter. Other researchers observed similar effects during drying of silane gels with the use of pyrene or ruthenium complex [18,30].

In the gel of pH 5.9 prior to drying, the domain of lifetime of about 40 ns was attributed to the excimer or the probably existing excimer-like ground-state pyrene aggregates.

Table 1
The lifetime of pyrene as a function of removed water and ethanol moles during drying of gel of pH 4.1

n (mol)[a]	$\lambda_{em} = 392$ nm			$\lambda_{em} = 467$ nm	
	Amplitude	τ (ns)	%	Amplitude	τ (ns)
0	0.40	11.35 ± 1.18	10.30	−0.52	47.75 ± 1.73
	0.59	55.08 ± 3.86	88.60	0.47	80.52 ± 1.87
0.00228	0.46	8.78 ± 1.65	11.20	−0.45	66.13 ± 1.05
	0.53	54.77 ± 2.09	87.80	0.54	100.57 ± 1.54
0.00552	0.45	10.27 ± 1.45	5.82	−0.45	69.73 ± 2.80
	0.53	135.30 ± 1.89	93.18	0.53	125.46 ± 2.43
0.00871	0.43	10.88 ± 0.92	4.36	−0.43	51.36 ± 4.30
	0.56	183.20 ± 2.58	94.64	0.56	202.36 ± 6.15
0.01190	0.43	9.85 ± 2.12	3.90	−0.48	53.47 ± 8.71
	0.56	183.10 ± 2.19	95.10	0.51	190.90 ± 1.86
0.01505	0.44	10.21 ± 0.98	4.30	−0.46	53.88 ± 5.23
	0.55	187.80 ± 1.68	94.70	0.53	197.55 ± 1.67
0.01805	0.29	9.72 ± 1.03	2.33	−0.55	42.26 ± 1.62
	0.70	166.30 ± 1.97	96.67	0.44	203.30 ± 2.93
0.02193	0.16	11.37 ± 1.22	1.35	−0.47	56.49 ± 4.01
	0.83	155.9 ± 1.22	97.65	0.52	182.33 ± 5.53
0.02590	0.99	146.70 ± 1.24	99.00	−0.55	46.71 ± 2.96
				0.44	187.20 ± 5.07
0.02977	0.99	154.30 ± 1.73	97.54	−0.45	56.22 ± 3.60
				0.54	166.77 ± 4.20
0.03255	0.99	147.10 ± 3.67	98.75	−0.46	46.90 ± 2.67
				0.53	158.90 ± 1.43
0.03629	0.12	47.41 ± 1.41	6.59	−0.46	47.52 ± 1.32
	0.86	163.10 ± 1.83	91.29	0.53	154.70 ± 1.89
0.04076	0.10	52.83 ± 1.05	2.95	−0.46	50.28 ± 3.05
	0.89	159.00 ± 3.25	94.10	0.53	144.20 ± 3.70
0.05280	0.10	33.52 ± 1.06	1.97	−0.25	44.08 ± 0.94
	0.89	140.40 ± 1.68	97.58	0.73	136.90 ± 1.40

[a] $n_0 = 0.05280$ mol—the initial number of moles of the water–ethanol mixture.

The lifetime of about 30 ns with a negative pre-exponential factor, shorter than in the gel of pH 4.1, would be related then to the dynamically formed probe aggregates and resulted probably from the interaction of pyrene with the surroundings in smaller pores of the gel cell than in the case of gel with pH 4.1. According to many authors, formation of ground-state pyrene aggregates is possible in the conditions of local increase of pyrene concentration and at higher viscosity, and also as a result of minimisation of the contact area of hydrophobic pyrene molecules with, for example the surrounding polar water molecules [24,33]. In the case of silane gels also silanol groups that are present on the surface of a gel cell interact with hydrophobic probe molecules and affect their aggregation [27,31].

In gels of pH 4.1 and 5.9 after subsequent drying stages prolonged probe lifetimes were observed (Tables 1 and 2). These lifetimes were used to approximate the fluorescence decay curves at both 392 and 467 nm. Similar effects were reported during drying of silane films in the air [18] or at the temperature of 50–300 °C [30]. For the gel of pH 4.1, the population of isolated pyrene molecules of decay time 185–200 ns and dynamically formed excimer of lifetime 50 ns dominated after the initial drying, i.e. after removal of about 0.008 mol of water and ethanol mixture. The 10 ns lifetime, observed during monomer fluorescence decay at the first stage of drying (n = 0–0.02 mol, Table 1), was attributed to a small content of ground-state pyrene dimers. The removal of portions of solvent vapours in the amount of over 0.02 mol, was connected again with shortening of the lifetime of monomer form of pyrene up to the value of 140 ns recorded in the pores of dry xerogel. The final tendency of shortening the probe lifetime was related to quenching of pyrene fluorescence by the gel net which—due to drying—contained still smaller gel pores free from solvent molecules. In this case the interaction of pyrene molecules with adsorbed water molecules on the pore surface was also possible [19].

In the gel of pH 5.9 a small domain of the lifetime 10 ns was observed at $\lambda_{em} = 392$ nm in the entire drying process. Besides, shortening of the lifetime of pyrene monomer form to about 198 ns started after the removal of a smaller amount of solvents, i.e. about 0.010 mol. This might be an evidence of really smaller pores in the gel of pH 5.9, as compared to the gel of pH 4.1. In xerogel, i.e. after removal of the last portion of the vapours of solvent mixture, two domains of lifetimes similar to those before drying, i.e. 30 and 50 ns, were identified for $\lambda_{em} = 467$ nm. They refer most probably to the dynamic formation of excimer-like pyrene and the

Table 2
The lifetime of pyrene as a function of removed water and ethanol moles during drying of gel of pH 5.9

n (mol)	$\lambda_{em} = 392$ nm			$\lambda_{em} = 467$ nm	
	Amplitude	τ (ns)	%	Amplitude	τ (ns)
0	0.30	11.60 ± 0.52	10.65	−0.45	29.82 ± 2.18
	0.69	42.74 ± 2.61	88.35	0.54	39.14 ± 1.76
5.57017E-4	0.30	42.42 ± 2.34	87.28	−0.55	35.92 ± 1.49
	0.69	86.49 ± 1.23	8.07	0.44	56.44 ± 1.23
0.00121	0.24	58.12 ± 1.42	46.38	−0.47	32.47 ± 1.26
	0.69	88.81 ± 2.21	50.74	0.52	89.45 ± 1.07
0.00167	0.12	53.14 ± 1.50	8.05	−0.45	50.92 ± 1.67
	0.80	122.30 ± 3.51	90.31	0.50	125.7 ± 1.49
0.00232	0.07	46.29 ± 1.10	3.37	−0.51	53.89 ± 2.40
	0.87	140.02 ± 1.50	95.34	0.48	124.59 ± 3.31
0.00288	0.37	13.73 ± 0.82	7.02	−0.53	35.57 ± 1.95
	0.62	92.17 ± 2.53	91.98	0.44	114.45 ± 2.63
0.00427	0.32	10.36 ± 0.12	2.58	−0.53	45.22 ± 2.44
	0.67	189.5 ± 3.90	96.42	0.45	155.12 ± 1.36
0.00473	0.30	11.39 ± 1.30	2.79	−0.52	54.34 ± 3.08
	0.69	177.30 ± 2.54	96.21	0.44	182.75 ± 4.68
0.0052	0.29	10.04 ± 0.53	2.11	−0.53	53.93 ± 1.72
	0.70	193.80 ± 3.62	96.89	0.46	196.92 ± 2.74
0.00706	0.30	10.48 ± 0.23	2.25	−0.53	53.75 ± 1.87
	0.69	195.30 ± 2.53	96.76	0.46	198.01 ± 2.42
0.01068	0.34	10.43 ± 0.34	3.27	−0.51	57.14 ± 2.75
	0.60	173.20 ± 1.34	95.73	0.48	189.09 ± 4.04
0.02247	0.34	11.05 ± 0.64	3.27	−0.53	51.44 ± 1.99
	0.65	180.4 ± 2.92	95.73	0.45	189.35 ± 3.20
0.02330	0.35	11.12 ± 0.32	3.36	−0.53	52.64 ± 2.39
	0.64	174.00 ± 1.74	95.64	0.46	178.3 ± 3.72
0.03054	0.36	10.82 ± 0.63	3.69	−0.53	52.20 ± 2.36
	0.63	160.9 ± 2.94	95.31	0.44	169.07 ± 3.57
0.04020	0.36	10.79 ± 0.74	3.95	−0.53	51.49 ± 2.68
	0.63	147.10 ± 1.43	95.05	0.46	146.13 ± 3.86
0.04735	0.35	13.77 ± 0.84	6.43	−0.52	46.88 ± 3.12
	0.64	105.70 ± 2.93	92.57	0.45	106.91 ± 3.90
0.04852	0.35	10.35 ± 1.68	6.87	−0.52	36.45 ± 1.94
	0.64	56.88 ± 0.34	92.13	0.47	50.12 ± 0.74
0.04970	0.34	10.65 ± 1.23	8.31	−0.52	26.87 ± 0.63
	0.65	47.23 ± 1.62	90.69	0.47	40.12 ± 1.09
0.05180	0.33	10.22 ± 0.89	8.88	−0.52	26.32 ± 1.63
	0.66	44.55 ± 1.52	90.12	0.46	40.45 ± 1.21
0.05280	0.40	9.867 ± 0.32	10.75	−0.52	32.41 ± 4.90
	0.59	51.59 ± 1.40	88.25	0.47	50.47 ± 5.10

presence of ground-state probe aggregates as a result of a significant reduction of the pore volume and shapes under the influence of drying.

When comparing final results of pyrene lifetime distributions in xerogels of pH 4.1 and 5.9, i.e. for $n = 0.0528$ mol (Tables 1 and 2), it can be seen that dry gel of pH 5.9 is characterised by a different structure than xerogel which was formed from sol of lower pH. The results of luminescence studies confirm the results concerning the structure of gels and xerogels made by other techniques [16]. Taking into account the composition of tested sols which differed only by pH, the same concentration of the applied fluorescence probe and identical conditions in which the gels were dried in oxygen-free atmosphere, a conclusion may be drawn that the fluorescence methods are suitable for testing changes that occur during formation of gels and xerogels of different structures depending on the pH of sol.

3.3. Model drying

The aim of studies on steady-state and time-resolved fluorescence was to describe changes that took place in the closest micro-surroundings of pyrene in the gel being dried. Selected gels were obtained in cells made from special optical glass, closed with a stopcock, in deoxygenated conditions (under vacuum), because a fluorescence probe applied was pyrene which is quenched by oxygen. The gels were stored in these air-tight cells, at constant temperature of 20 °C. The samples were connected to the vacuum line cyclically to remove some amount of solvent vapours recorded at

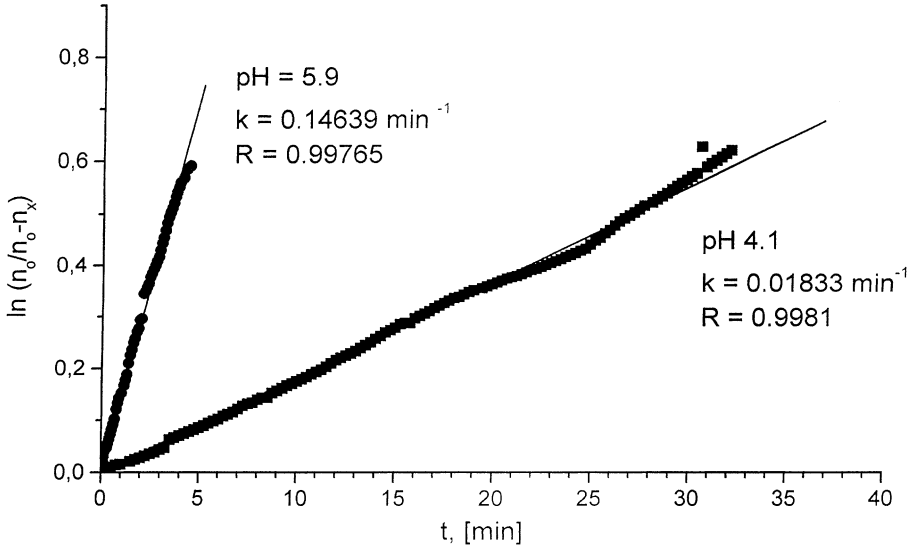

Fig. 6. The kinetics of gels drying.

constant temperature in time as a pressure change on a mercury barometer. Under a simplifying assumption that the mixture of water and ethanol vapours satisfies the state equation of ideal gas and knowing the volume of the measuring system, pressure changes were converted into moles of n mixture of water and ethanol vapours. Results obtained, particularly in the initial stage of model drying, are best described by the first-order kinetics according to the equation:

$$\ln \frac{n_0}{n_0 - n} = kt$$

where n_0 is the initial amount of water and ethanol in the sample equal to 0.0528 mol, n the quantity of solvents removed after time t, k (min^{-1}) the model drying rate constant.

Experimental results are shown in Fig. 6. So defined drying of porous silane gels involves removal of unbound water and ethanol from the carrier pores [31,34]. The adsorbed water molecules on the gel cell surface, can be removed only by heating of the sample which was shown in fluorescence studies concerning vacuum drying of silane gels using pyranine [34] or ruthenium complex [30].

Drying rate constants were determined on the basis of experiments. They are $k = 0.01833\,\text{min}^{-1}$ for the gel of pH 4.1, and k=0.14639 min^{-1} for the gel of pH 5.9, respectively. An almost 10 times higher drying rate constant for the gel of a higher pH was attributed to the porous structure of this gel as compared to the gel of pH 4.1. The colloidal structure of xerogel of pH 5.9 facilitated the removal of solvent molecules. The results are in agreement with the above described results of time-resolved and steady-state fluorescence measurement of dried gels.

Also research carried out in the process of gel formation [22] confirmed that gel obtained from the sol of lower pH had higher porosity which was a result of a changing ratio of relative rates of hydrolysis and condensation in the gel being formed depending on pH of the sol [16].

4. Summary

Silane gels based on TEOS, obtained by the sol–gel method were dried in the oxygen-free atmosphere. The process was monitored using fluorescence techniques. It was found that at the first stage, the model drying was best described by the first-order kinetics. The rate constant determined for gel drying at pH 5.9 was 10 times higher than for the gel of a lower pH value. With an increase of the quantity of water and ethanol vapours removed from the gel, also a decrease of polarity was observed in the carrier pores, up to the final value which was different depending on the gel structure. An increase of the excimer intensity during drying was attributed to the loss of solvent molecules in the gel pores, and also to a decrease and deformation of xerogel pores, particularly in the final stage of drying of the xerogels.

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