

# Raman system for on-line monitoring and optimisation of hybrid polymer gelation

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*Authors designed and built a Raman spectroscopic system for non-invasive, remote, on-line monitoring of gelation, which is the first step of a sol-gel process used for synthesis of hybrid polymers for photonics. The system was connected with typical glass reaction vessel. Suitable design of an optical system reduced excitation of interfering Raman signal in the wall of the reactor. Application of two excitation wavelengths reduced influence of fluorescence on measurements and provided high efficiency of the Raman system in wide range extending from 200 to 3500 cm<sup>-1</sup>. Synthesised materials were based on silane precursors having epoxy and amino functionality. Raman spectroscopy enabled strict control over molecular structure of the materials during the polymerization process. Time and efficiency of monomers hydrolysis were measured. Products of this reaction were evaluated. The obtained data enabled us optimisation of the process parameters which ensured high efficiency of hydrolysis and subsequent control of solution viscosity. Moreover, behaviour of amine groups and epoxy rings was investigated and influence of water and solvents was found.*

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## 1. Introduction

Raman spectroscopy is a powerful and versatile research technique with a broad range of potential applications for industrial process control. Its scope of use in on-line process monitoring is limited by the fact that the measurement has to be performed on substances present in the processing equipment, rather than on a preconditioned sample using equipment which in most cases cannot operate in the production environment. As a result, the measurement equipment has to be located remotely from the processing equipment and a means of introducing intense laser light to the process equipment and collecting Raman scattered light have to be found. Addressing industrial requirements, robust and cost-effective Raman setups should be developed to enhance application field of this technique. Moreover, each particular application requires reliable analysis of measurement conditions and subsequent Raman system adaptation.

One of the most important field of Raman measurements use is development of new materials for photonics and other advanced technical applications. Requirements of modern photonics stimulate search of materials which have improved optical, mechanical and electrical properties. Consequently, several materials are being developed and

synthesised using different technological processes. However, one of the most modern trends in material science is development of whole groups of materials whose properties can be changed in a wide range by suitable design of their molecular structure. Such a group of materials should be synthesised in the same technological process, while their properties are controlled by slight modifications of the synthesis parameters.

Organically modified silanes (ORMOSILs) prepared in the sol-gel technology are one of the groups based on this concept. Incorporation of organic components into an inorganic silica network can provide coincidence of advantages of both groups of materials. In comparison with organic materials, hybrids have better thermal stability, scratch resistance and hardness, while their toughness and flexibility is better than properties of glasses. Moreover, ORMOSILs' workability is very good.

Hybrids can be used in photonics to manufacture planar waveguides, lenses, Bragg gratings and components for integrated optics. Moreover, dielectric layers, coatings and packaging are produced from these materials. Research to apply them in optical fibre sensors (including bio-sensors) and solid state lasers is underway [1–5].

The main advantage of the sol-gel technology is the possibility of synthesis of sophisticated materials in a relatively simple, cost-effective and low-temperature process. This method enables us precise control of a precursor com-

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position as well as optical and mechanical properties of the final product. Sol-gel allows one to connect organic components, which can be decomposed at high temperatures with inorganic ones which have high thermal resistance. The most important drawbacks of sol-gel technology are: high cost of some of precursors and low resistance of a product to the temperatures higher than several hundreds degrees centigrade.

Investigation of the sol-gel synthesis process of ORMOSILs is a very difficult task because of complex molecular structure of materials. On the other hand, precise control of the structure must be ensured during production to obtain required properties of the hybrid material. This stimulates development of advanced systems for remote, non-invasive monitoring of a technological process. Raman measurements can be applied to characterise hybrid polymers and provide very useful information about chemical structure of components and final products as well as progress, correctness and efficiency of the technological process. Subsequent steps of the sol-gel process, from precursor hydrolysis through condensation and film deposition to the production of optical components, can be investigated [4–7].

In this paper, Raman spectroscopic studies carried out for on-line monitoring of the most important reactions, which take part during gelation – the first step of sol-gel process, are presented. Development of Raman system for *in-situ* monitoring of the sol-gel process is the following, more advanced stage of research presented elsewhere [6].

## 2. Principles of Raman spectroscopy

Raman spectroscopy is based on recording and spectral analysis of radiation scattered inelastically by the investigated object [8]. As a result of interaction between monochromatic light and dipoles induced in an oscillating molecule, transition of the molecule from the initial energy level, through an excited virtual state, to the energy level different from the initial one, may take place. Photons observed in scattered light may have energy lower or higher than in an incident beam which is called Raman scattering in a Stokes or anti-Stokes band, respectively. The difference between wavelengths of photons in the incident ( $\lambda_0$ ) and the scattered light is known as a Raman shift. It is related to characteristic oscillation frequencies of the molecule. It can be the oscillations of a single molecular bond or the larger fragment of a polymer network. For the specified excitation wavelength  $\lambda_0$ , Raman intensity can be expressed as [8]

$$I_R = I_L \sigma K P C, \quad (1)$$

where  $I_R$  is the measured Raman intensity (photons per second),  $I_L$  is the laser excitation intensity (photons per second),  $\sigma$  is the absolute Raman cross-section ( $\text{cm}^2$  per molecule),  $K$  is the constant accounting for measurement parameters,  $P$  is the sample path length (cm), and  $C$  is the concentration (molecules per  $\text{cm}^3$ ).

The analysis of vibrational spectra of hybrid polymers is a difficult task because of their complex chemical structure. Characteristic Raman shifts depend on neighbourhood of the group of atoms as well as their position in molecule or polymer network. Moreover, the peaks assigned to coupling and resonance between a single oscillation may also appear in the spectrum.

Selection of the optimal excitation laser wavelength  $\lambda_0$  is a very important problem in Raman spectroscopy. Basically, for  $\lambda_0$  far from molecule absorption band, intensity of the Raman signal is inversely proportional to  $\lambda_0^4$  so application of a VIS or UV laser as the excitation source should more effective than an IR one if the intensity of Raman scattering was considered. However, practical efficiency of Raman scattering versus excitation wavelength may also depend on dimensions of the investigated structures.

Moreover, fluorescence induced by the laser beam must be also taken into account. Fluorescence is the strongest for the excitation wavelength  $\lambda_0$  range extending from 270 to 700 nm [9] but its influence can be different for various materials. It is particularly strong for organic materials, so the excitation range in VIS and near UV is not appropriate for their investigation. Moreover, application of excitation in UV increases the price of equipment compared to system working in VIS-NIR range and the possibility of catalysis of unwanted photochemical reactions which interfere with the investigated technological process.

Application of NIR lasers (785–1064 nm) causes the problems with selection of detector types that can ensure high efficiency of the measurement system in a wide Raman range, required in hybrid polymer investigation. This range is limited by skeletal vibrations of polymer networks ( $250\text{--}500\text{ cm}^{-1}$ ) and N-H stretching ( $3300\text{--}3400\text{ cm}^{-1}$ ) [6,10]. Silicon detectors are not sensitive enough to record a scattering signal in a wavelength range above 1  $\mu\text{m}$ , that results in limitation of Raman range to about  $2800\text{ cm}^{-1}$  for excitation wavelength equal to 785 nm. Regarding InGaAs detectors, as their high efficiency can be obtained in a wavelength range of above 900 nm, Raman range of systems using such detectors begins at about  $800\text{ cm}^{-1}$  for excitation wavelength equal to 830 nm. Application of InGaAs and Ge detecting systems stimulates the use of lasers of wavelength higher than 880 nm that might decrease efficiency of Raman scattering in the investigated material. Moreover, price of InGaAs and Ge detectors, higher than Si ones, may significantly increase the cost of the Raman measurement system.

Considering the problems presented above, excitation wavelengths in our measurements were selected in experimental way, by the comparison of spectra recorded for different excitation wavelengths.

## 3. Experimental

### 3.1. Procedure of investigated gelation

The synthesised polymer belongs to the group of hybrid organic-silicate materials and was prepared using hydrolytic sol-gel route. In the process presented in this paper, two

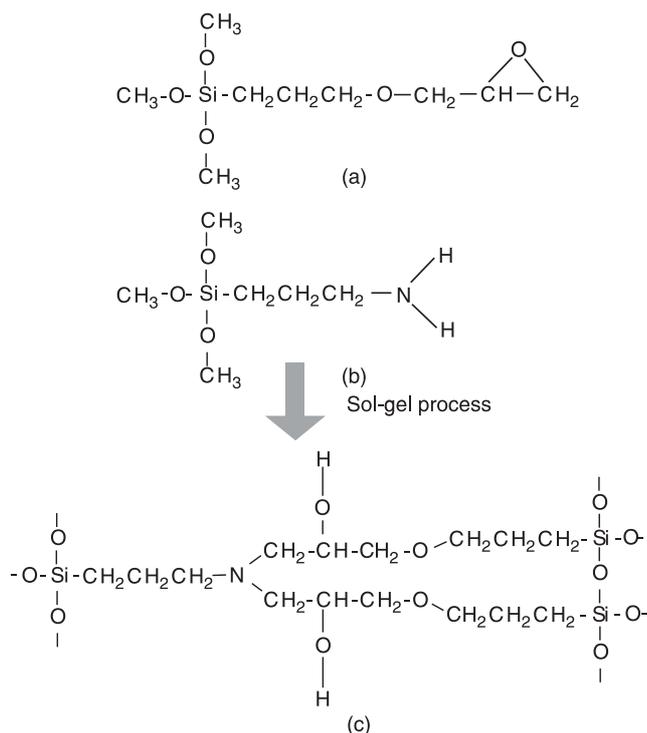


Fig. 1. Molecular structure of (a) GPTS, (b) APTES, and (c) expected product of the process.

commercially available precursors: 3-glycidoxypropyl-trimethoxysilane (GPTS) and 3-aminopropyl-trimethoxysilane (APTES) were used for synthesis. Molecular structure of precursors as well as the expected polymer network is shown in Fig. 1.

The system was equipped with a two-neck round bottom glass reaction vessel and a magnetic stirrer. In the first step, set of solvents – acetone (Ac) and methylisobutylketone (MiBK) – was added to a mixture of GPTS and APTES. The solution was stirred for 10–15 minutes. Subsequently, distilled water was added dropwise to the solution to initialise hydrolysis and the resulting solution was mixed for 23 hours. Regarding inorganic part, the aim of gelation was to cause the replacement of the alkoxy group by the hydroxyl group followed by the creation of the siloxane structures and, subsequently, inorganic network. The main aim of investigation was to find optimal ratio of the silanes, water and solvents that ensure efficiency of hydrolysis of about 100% for a system maintained in liquid form as well as to investigate reactions in an organic part.

Regarding the organic part, it was expected that primary amine – APTES – would turn to tertiary one. Moreover, opening of epoxy rings was predicted. They were to be the basic reactions for organic polymerisation.

At the beginning, the ratio of components as well time of particular reactions was predicted theoretically. During the investigation, volumes of materials as well as time of reaction were the subjects of optimisation.

### 3.2. Raman characterisation of the process

To address the problem of real-time monitoring of a sol-gel synthesis process, the authors developed a Raman scattering measurement system coupled with a glass reaction vessel by an optical fibre bundle. Two-neck vessel of a volume equal to 50 ml was the mostly common used one. The presented Raman devices were also tested for the smaller, one-neck vessel of a volume equal to 10 ml. The measurement set-up is presented in Fig. 2(a). Application of a micrometric three-dimensional positioning system enabled effective optical coupling between the reaction vessel and the Raman probes as well as precise adjustment of the optical measurement system. Suitable design of the opto-mechanical system made the measurements independent of a change of the liquid volume during the reaction.

Measurements presented in this paper were made in a Raman range extending from  $200\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$ . Two wavelengths of the excitation laser beam were tested, i.e., 720 nm and 830 nm. For the shorter one, a strong fluorescence, induced by laser beam, appeared at the Raman range below  $2000\text{ cm}^{-1}$ . Excitation of 830 nm did not provide suitable efficiency of scattering signal collection at the

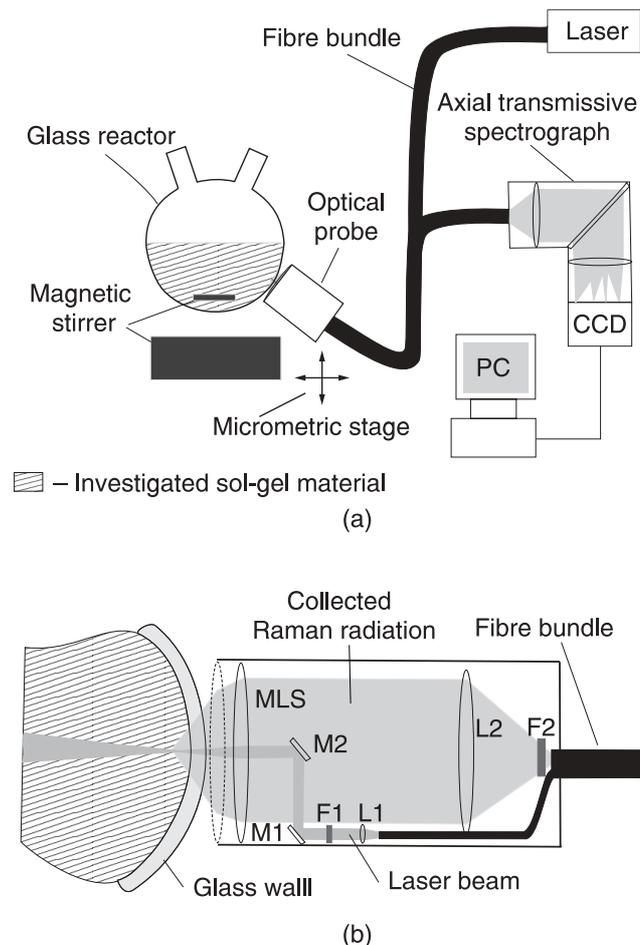


Fig. 2. Raman system for process on-line monitoring: (a) general diagram and (b) system for optical coupling between Raman system and reaction vessel.

Raman range above  $2000\text{ cm}^{-1}$  when a silicon CCD detector array was used.

To eliminate these problems, the authors devised two complementary Raman systems that uses excitation wavelength 720 nm and 830 nm. The system for measurements in Raman range extending from  $200\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$  was based on the CCD-spectrometer Ramstas, developed at the VTT Electronics [11]. Excitation wavelength of 830 nm was used. In order to determine the required power of a laser beam on the sample, measurements were carried out for the highest level (135 mW) with acquisition time equal to 8 or 10 s as well as for the reduced power level (55 mW) and acquisition time of 15 s. Ramstas is equipped with an axial transmissive spectrograph using a transmission holographic grating (wavelength range from 850 to 1000 nm) as well as with a TE-cooled silicon CCD detector array [11]. The spectral resolution was equal to  $8\text{ cm}^{-1}$ .

Fully dedicated system was designed and build by the authors for measurements performed in the Raman range above  $2000\text{ cm}^{-1}$  with the spectral resolution of  $8\text{ cm}^{-1}$ . A Ti:Sapphire laser pumped by an Ar:Ion laser was used as an excitation source. Wavelength was tuned to 720 nm. Power on the sample was 50 mW while acquisition time equal to 30 s or 60 s was used. An axial transmissive spectrograph using transmission holographic grating (wavelength range from 850 to 1000 nm) and a TE-cooled silicon CCD detector array were used in the detection part.

The main disadvantage of the Raman system that uses simultaneously two excitation wavelengths is the optical interference between both sub-systems. Because of this reason, time-division measurements should be carried out. Moreover, although the same spectrometer can be used in both systems, separated probes have to be applied, because different optical filters are used.

Both systems were equipped with fibre optic probes including dedicated focusing lens system. A set-up of a fibre optic probe as well as its connection with reaction vessel is presented in Fig. 2(b). Excitation laser radiation is transmitted through a single fibre and collimated by the lens L1. A bandpass filter F1 cuts off fluorescence while two mirrors M1 and M2 and multi-lens system MLS ensure transmission and focusing of laser beam inside glass vessel. A dedicated multi-lens system MLS of a provided tunability of a focal length in the range extending from 1.25 to 2.5 cm was used for focusing a laser beam inside the vessel and collecting a scattering signal. As a result of careful optimisation of MLS design it is possible to avoid excitation of interfering Raman scattering in a glass wall of the flask for a broad range of wall thickness and vessel diameters. Moreover, the operation of the system was independent of liquid volume change during the reaction. A focal point was adjusted, using the micrometric three-dimensional positioning system and MLS, to obtain high intensity of a Raman line at  $637\text{ cm}^{-1}$  assigned to silanes and to eliminate a band at  $450\text{ cm}^{-1}$  originated from the glass wall. As the liquid inside the flask was stirred with high velocity (about 700 revolutions per minute), it was assumed that the results

of measurements carried out in one point are representative for the whole volume of the sol. Part of the scattering signal collected by MLS is filtered by the filter F2 that cuts off Rayleigh scattering signal, while Raman signal in a Stokes band is transmitted. The lens L2 focuses scattering radiation into a fibre bundle that transmits it to the spectrometer.

To monitor the process, Raman spectra were acquired at regular time intervals, sufficient for the process dynamic. Further in this paper, it is referred to as kinetic series. For sol-gel processes presented in this paper, Raman spectra were recorded during 23 hours with repetition ratio at least 1 acquisition per minute and, simultaneously, viscosity of the solutions was monitored by visual means.

Two background correction procedures were applied. Signal originating from external illumination was recorded before the start of each monitored process with the time of acquisition equal to the time of subsequent acquisition of the Raman signal. Data processing software subtracted the signal representing external illumination from each recorded Raman spectrum. This procedure enabled Raman monitoring even in moderately illuminated laboratory. Other source of background was fluorescence of material induced by laser radiation. A level of this signal for every investigated Raman line was determined basing on acquired Raman spectrum. It had to be considered that sensitivity of the detecting system is a function of wavelength and consequently the recorded fluorescence signal varies, not rapidly, in dependence on a wavelength. However, the number of investigated Raman lines was limited and fluorescence level was constant in immediate neighbourhood of each of them. The authors decided to simplify data processing by arbitrary selection of wavelength in the immediate neighbourhood of each Raman line. These wavelengths were selected in this parts of the spectrum, in which contribution of Raman lines was negligible and they were assumed to be representative to fluorescence level for respective Raman lines. As fluorescence varies also in dependence on reaction time, for each spectrum in the kinetic series intensity of the wavelengths representative for fluorescence was subtracted from the intensity of respective Raman line intensity. Further, in this paper, this procedure is referred to as dynamic subtraction of a background.

An amplitude of the Raman bands was used in quantitative data analysis. The use of integral intensity of the bands was not required as the changes of width (FWHM) of the most important lines in the recorded spectra were not noted during the investigated processes. Moreover, as only slight changes of fluorescence as well as small fluctuations of intensity of the Raman bands, caused by fluctuations of the laser power and external illumination, were noted the use of reference Raman band in intensity studies was not required.

To confirm the obtained results, Raman spectra of precursors and products were also recorded with FT-Raman system BioRad FTS6000 that uses Nd:YAG laser beam (1064 nm) of a power on sample equal to 450 mW as an excitation source.

## 4. Results of investigation

### 4.1. Basic reactions for inorganic polymerisation

At the primary level of process studies, the calculated volumes of materials were assumed to be appropriate ones and were used for synthesis as follows: 16.25 ml (0.074 mol) of GPTS, 5.2 ml of APTES (0.029 mol), 13 ml of solvents (volume ratios for Ac:MiBK were 3:1, respectively) and 2.78 ml of distilled water (0.154 mol). Molar ratios for GPTS, APTES and water were 2.5:1:5.25, respectively. This system is referred to as sol no. 1 further in the paper. The molar ratio between silane precursors remained constant through all the experiments.

Raman spectra in the range extending from  $200\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$  are presented in Fig. 3. A doublet at  $606\text{ cm}^{-1}$  and  $637\text{ cm}^{-1}$  can be assigned to asymmetric and symmetric stretching  $\nu(\text{Si}(-\text{O}-\text{CH}_3)_3)$ , respectively. This doublet is characteristic for non-hydrolysed trimethoxysilane molecules [6,7]. A kinetic plot of intensity of this doublet is shown in Fig. 4 (part a and b). Kinetic plots are corrected by dynamic subtraction of background that can be seen in the spectra presented in Fig. 3. After 22 hours of mixing, the doublet at  $606\text{ cm}^{-1}$  and  $637\text{ cm}^{-1}$  disappeared, therefore it can be concluded that hydrolysis efficiency equal to 100% was obtained, while the system was maintained in a liquid and transparent form. Wide band at  $484\text{ cm}^{-1}$ , assigned to  $\text{SiO}_2$  network, has appeared. It confirmed the beginning of an inorganic network condensation. A band at  $1031\text{ cm}^{-1}$  can be assigned to methanol which was a by-product [6,7].

In order to confirm the obtained results, additional gelation processes were carried out for sol no. 1. Raman spectra recorded in the range extending from  $200\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$  during the first confirmation gelation of sol no. 1 are presented in Fig. 5. A kinetic plot of a decrease in doublet at  $606\text{ cm}^{-1}$  and  $637\text{ cm}^{-1}$ , corrected by dynamic subtraction of background, is shown in Fig. 6. It appeared

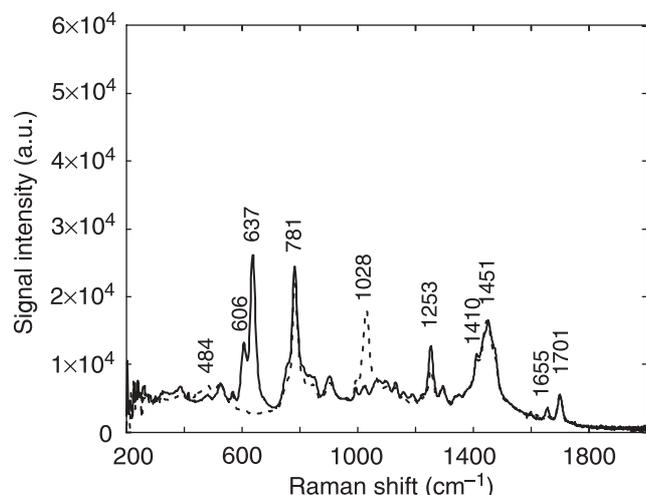
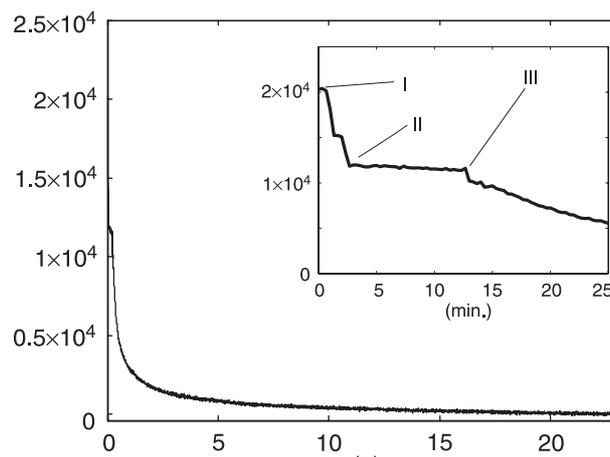
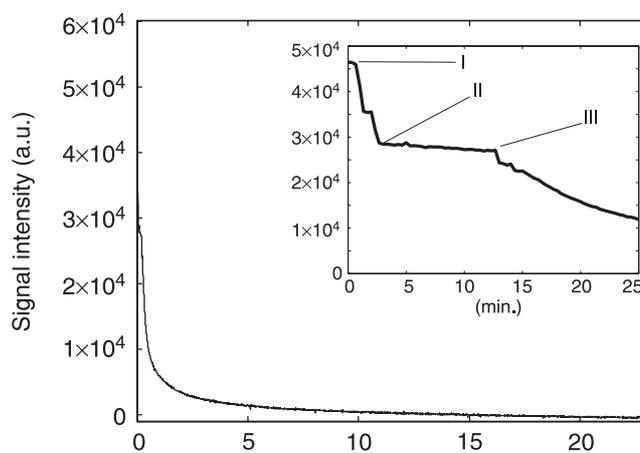


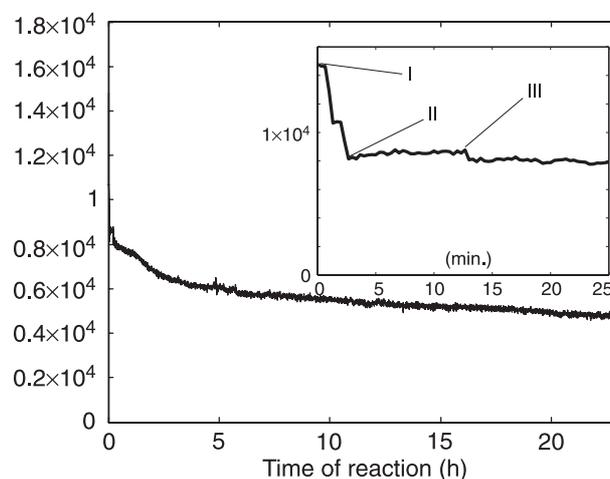
Fig. 3. Raman spectra obtained during the first gelation of sol no. 1: constant line represents solution after addition of solvents and water, dashed line – product.



(a)



(b)



(c)

Fig. 4. Decrease in intensity of selected Raman bands during gelation of sol no. 1: (a)  $606\text{ cm}^{-1}$ , (b)  $637\text{ cm}^{-1}$ , and (c)  $1253\text{ cm}^{-1}$ ; insets show initial 25 min. of the process; following steps were marked: I – solution of silanes, II – mixture after addition of solvents, III – solution after addition of water.

that during the confirmation process, the system has become dense and subsequently turned to non-transparent solid after about 3 hours since water addition. A moment when the system becomes dense can be found because of a

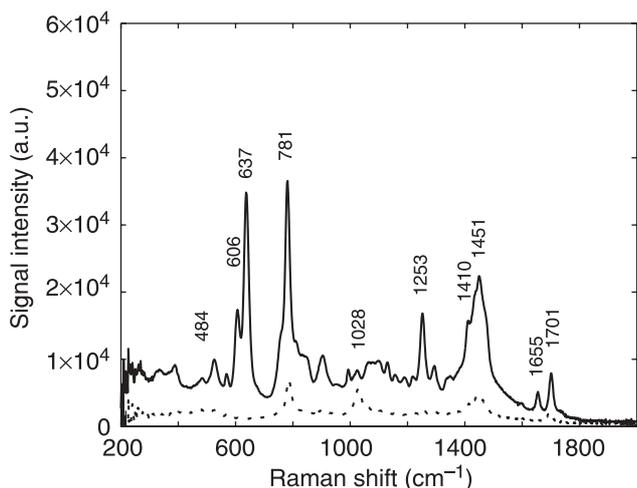


Fig. 5. Raman spectra recorded during confirmation gelation of sol no. 1. Constant line shows spectrum of solution after addition of solvents and water, dashed line – product.

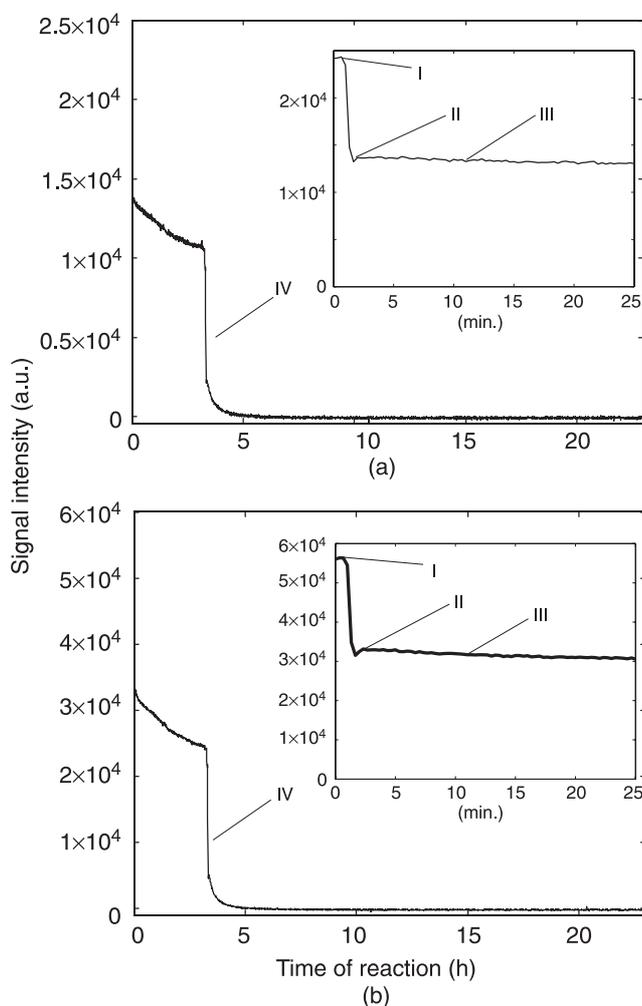


Fig. 6. Decrease in intensity of Raman bands assigned to stretching  $\nu(\text{Si}(-\text{O}-\text{CH}_3)_3)$  during confirmation gelation of sol no. 1: (a)  $606 \text{ cm}^{-1}$ , (b)  $637 \text{ cm}^{-1}$ ; insets show initial 25 min. of the process; following moments were marked: I – solution of silanes, II – mixture after addition of solvents, III – solution after addition of water, IV – turning solution to solid.

rapid decrease in all Raman lines intensity. Until this moment, efficiency of hydrolysis of about 20% was obtained, so the parameters of gel were insufficient. During the second confirmation measurement, sol started becoming dense after about 15 minutes since water addition.

Gelation of sol no. 1 proved to be very sensitive to the process parameters, probably mostly to a speed with which water was added. Amount of the solvents proved to be insufficient to maintain solution in a liquid form for the required time of reaction. It makes gelation of sol no.1 hardly repeatable. This situation stimulated optimisation of the ingredient ratio in order to ensure efficiency of hydrolysis equal to 100% while maintaining the solution in liquid and transparent form.

To solve the problem described above, a ratio of the solvents to other components was increased 2.5 times in comparison with sol no. 1. The following amounts of materials were used to prepare solution referred to as sol no. 2: 2.8 ml of APTES (0.016 mol), 8.75 ml of GPTS (0.04 mol), 17.5 ml of solvents and 1.5 ml of distilled water (0.083 mol).

Raman spectra recorded in the range extending from  $200 \text{ cm}^{-1}$  to  $2000 \text{ cm}^{-1}$  during gelation of gel no. 2 are presented in Fig. 7. A kinetic plot of intensity of the peaks at  $606 \text{ cm}^{-1}$  and  $637 \text{ cm}^{-1}$ , corrected by subtraction of a background, is shown in Fig. 8 (part a and b). The doublet at  $606 \text{ cm}^{-1}$  and  $637 \text{ cm}^{-1}$  disappeared after 22 hours of mixing. It can be concluded that hydrolysis efficiency equal to 100% was obtained. Wide band at  $484 \text{ cm}^{-1}$ , assigned to  $\text{SiO}_2$  network, confirmed the beginning of an inorganic network condensation. The band at  $1028 \text{ cm}^{-1}$  is assigned to methanol, which was a by-product. A solution maintained its transparent, liquid form up to next 48 hours. Two additional confirmation measurements were carried out and the same results were obtained. It showed that used amount of solvents was appropriate to obtain gel of parameters adequate for thin film deposition.

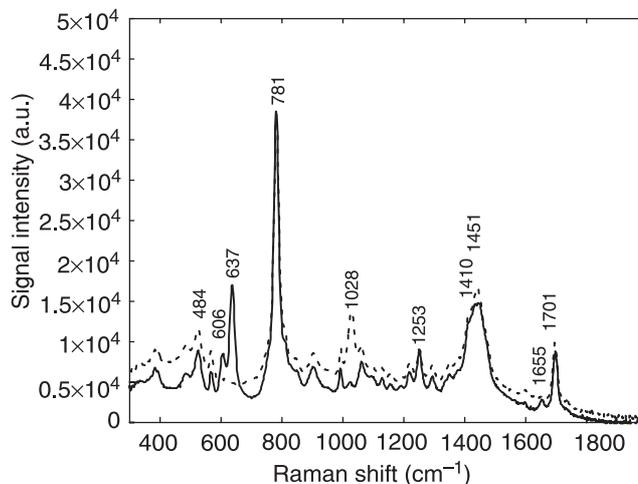


Fig. 7. Raman spectra obtained during the first gelation of sol no. 2: constant line represents solution after addition of solvents and water, dashed line – product.

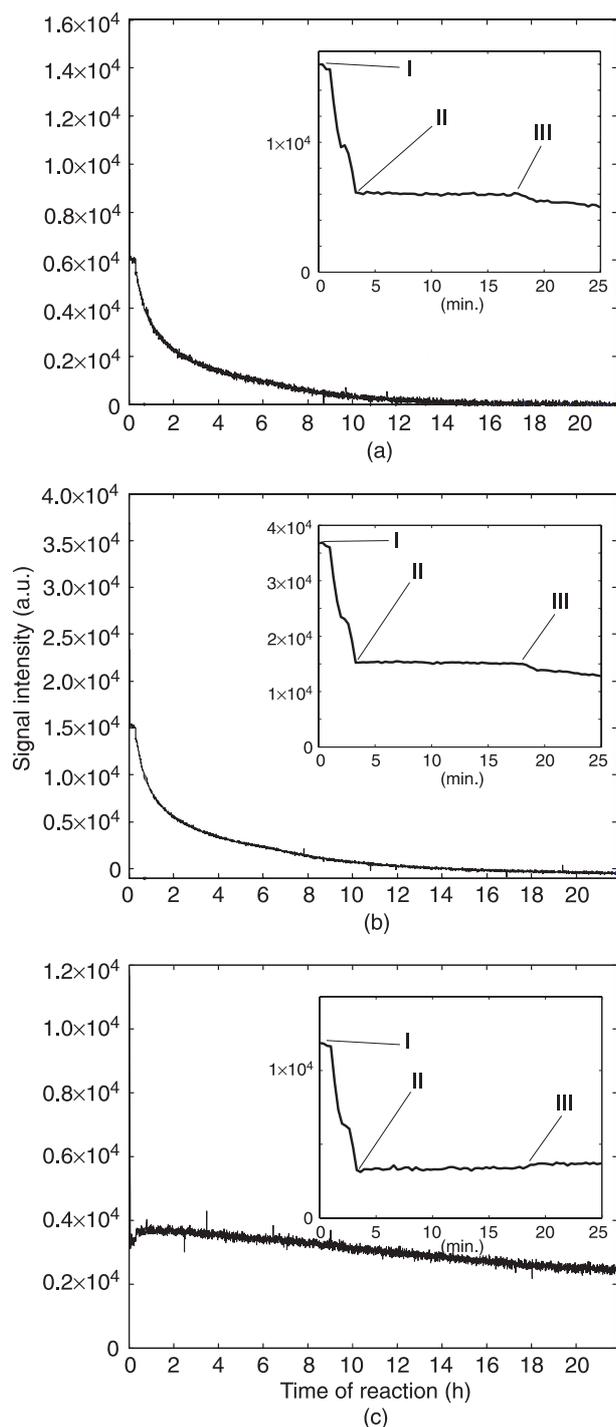


Fig. 8. Decrease in intensity of selected Raman bands during gelation of sol no. 2: (a)  $606 \text{ cm}^{-1}$ , (b)  $637 \text{ cm}^{-1}$ , (c)  $1253 \text{ cm}^{-1}$ ; insets show initial 25 min. of the process; following steps were marked: I – solution of silanes, II – mixture after addition of solvents, III – solution after addition of water.

## 4.2. Amine and epoxy reaction studies

The reaction between primary amine and epoxy ring was expected to be the most important one for organic polymerisation and therefore became the subject of studies during the research project presented in this paper. According

to the preliminary expectations, the reaction should have begun after mixing GPTS with APTES and proceeded quite rapidly.

A peak at  $1253 \text{ cm}^{-1}$ , which can be seen in Fig. 3, can be assigned to epoxy ring breathing of GPTS [10]. A kinetic plot of decrease in this line during gelation of sol no. 1, corrected by dynamic subtraction of background, is presented in Fig. 4(c). Contrary to expectations, Raman monitoring showed that process of epoxy ring opening proceeded slowly. Decrease in the intensity of the band at  $1253 \text{ cm}^{-1}$  shows that almost 40% of epoxy ring was opened during 23 hours of monitoring, however, reaction was not finished.

To study more precisely epoxy ring opening process, additional measurement was carried out for the system: 16.25 ml of GPTS, 5.2 ml of APTES, and 13 ml of solvents. This system is denoted in further part of the paper as sol no. 3. A kinetic plot of intensity of a peak at  $1253 \text{ cm}^{-1}$ , during the process carried out for this sol is shown in Fig. 9. The curve is corrected by subtraction of the background signal. Intensity of the band assigned to epoxy ring breathing was constant and quite large during the process.

A decrease in a Raman doublet at  $3310 \text{ cm}^{-1}$  and  $3370 \text{ cm}^{-1}$ , assigned to  $\text{NH}_2$  stretching [10], was used to study the primary amine – APTES – transformation. Results of measurements carried out in Raman range extending from  $3100 \text{ cm}^{-1}$  to  $3500 \text{ cm}^{-1}$  for sol no. 1 are presented in Fig. 10. Addition of GPTS to APTES did not initialise transformation of primary amine. It appeared that this transformation started after solvents had been added. However, after 10 minutes of stirring of a silanes/solvents system, transformation was not completed. After addition of water, it took about 2 minutes to obtain efficiency of amine transformation close to 100%.

Results of the Raman investigation showed that, in spite of the author expectations, catalysts were required to initialise amine transformation. Additional studies were car-

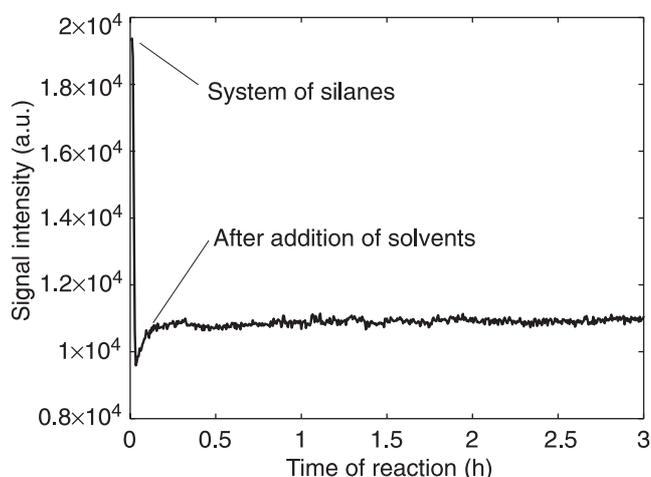


Fig. 9. Kinetic plot of intensity of the Raman band at  $1253 \text{ cm}^{-1}$  during gelation of sol no. 3.

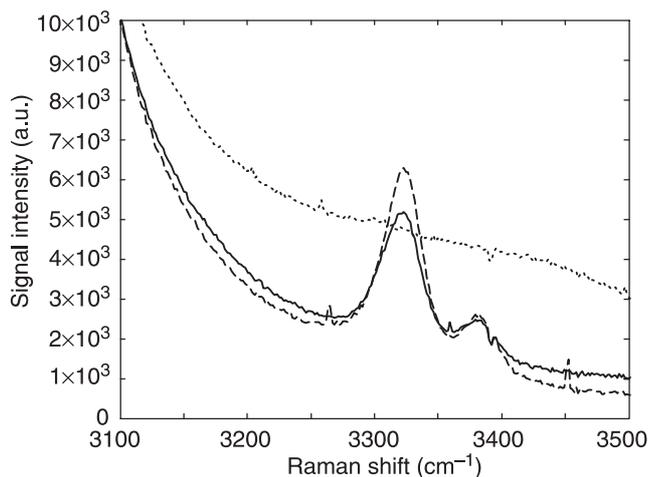


Fig. 10. Decrease in a Raman doublet at  $3310\text{ cm}^{-1}$  and  $3370\text{ cm}^{-1}$  during gelation performed for sol no. 1. Dashed line represents spectrum of silanes, constant line – solution just after addition of solvents, dotted curve – spectrum recorded 2 min. after addition of water.

ried out to find out which of the ingredients works as such a catalyst. Materials under the test were separately added to the sets of GPTS/APTES and solutions were mixed for 3 hours while Raman spectra were monitored in the range extending from  $2000$  to  $3500\text{ cm}^{-1}$ . The results showed that water and acetone can catalyse amine transformation while isopropyl alcohol cannot.

Decrease in the Raman doublet at  $3310\text{ cm}^{-1}$  and  $3370\text{ cm}^{-1}$  after addition of solvents during the process performed for the sol no. 2 is shown in Fig. 11. Dashed line presents spectrum of silanes, constant line – solution just after addition of solvents, dotted line – solution after transformation of primary and secondary amine, that took place, as it could be seen at the Raman spectra, about 3 minutes after addition of solvents. Increased ratio of ace-

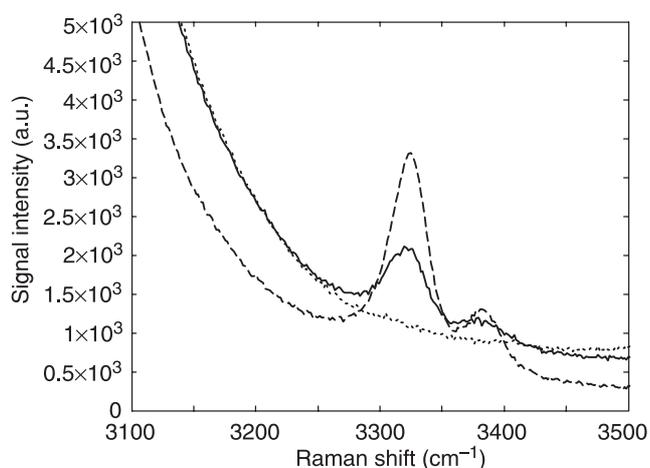


Fig. 11. Decrease in a Raman doublet at  $3310\text{ cm}^{-1}$  and  $3370\text{ cm}^{-1}$  during gelation performed for sol no. 2. Dashed line presents spectrum of silanes, constant line – solution just after addition of solvents, dotted line – solution after following 3 min.

tone was adequate for catalysis of full volume of APTES transformation.

Decrease in kinetic plot of the band assigned to epoxy ring during gelation of sol no. 2, presented in Fig. 8(c), showed that epoxy ring opening was also quite slow process and efficiency of almost 40% was obtained after 23 hours of mixing. However, reaction was not finished.

Results of Raman investigation showed importance of catalysts for primary amine and epoxy ring reactions. Moreover, significant difference in time of the reactions which were on-line measured, suggested that primary amine and epoxy rings did not react directly, but thorough additional reactions with other components. Moreover, it appeared that although both water and acetone were able to catalyse amine transformation, only water initialised the epoxy ring opening. Consequently, the process requires additional studies which can explain more precisely behaviour of epoxy rings as well as other reactions in organic part of the material. On-line Raman monitoring should make possible to determine an optimal set of solvents and time required for expected reactions.

## 5. Conclusions

Raman spectroscopy proved its considerable potential in technological process control and optimisation which provides development of advanced, high-quality materials of a structure designed on a molecular level. The optical systems for Raman measurements, presented in this paper, can remotely monitor a technological process performed in a typical glass reaction vessel. The measurement was completely non-invasive. As the access inside the vessel is not required, it is possible to use Raman spectroscopy also to control vacuum processes as well as those which are being performed in the presence of aggressive chemical atmosphere. Remote measurements can be carried out in clean-room conditions that are required for sol-gel synthesis of sophisticated optical materials.

Raman systems using diffraction gratings and CCD matrices seem to be very effective tool for kinetic measurements. A concept of two-wavelength excitation system ensured fluorescence-free investigation as well as the work of silicon CCD matrix in the spectral range of a high efficiency which is a low-cost solution in comparison with application of InGaAs arrays. Moreover, for some applications, the laser wavelength equal to  $720\text{ nm}$  can provide efficiency of Raman scattering excitation much better than NIR laser beam what is additional advantage of two-wavelength excitation system.

Results of measurements carried out with various laser power levels on the sample showed that the level of about  $50\text{ mW}$  is adequate for the systems using fibre optic probes, axial transmissive spectrographs, and CCD silicon matrices for both excitation wavelengths. It means that laser diodes of the output power equal to  $100\text{ mW}$  can be effective, low-cost excitation sources for the systems that can be used for sol-gel *in-situ* investigation.

Amount of ingredients required to ensure efficiency of monomers hydrolysis equal to 100% for solution maintained in liquid and transparent form were found. Moreover, optimal time of hydrolysis was measured with high precision. Gelation parameters were optimised to synthesise high quality gel that was suitable for deposition on a substrate and production of thin film of required structure of inorganic silane network.

The reaction of the epoxy and amine groups was recorded and described. Transformation of a primary amine was confirmed. However, the investigation results suggest that some other reactions, besides the amine-epoxy one, take place in an organic part of the solution. Importance of water and acetone for investigated reactions was found. Behaviour of primary amine and epoxy rings as well as importance of water and solvents will be the subject of further detailed studies.

For further studies more advanced tools for data processing will be developed. They will be based on representation of Raman bands by the Lorentz function and fluorescence as a polynomial as well as the use of reference Raman lines. It will make possible to apply Raman monitoring to the processes in which a fluorescence level or optical properties of the medium, i.e., refractive index or attenuation, significantly change during the reactions.

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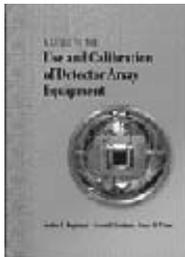
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