Macroporous monolithic materials: synthesis, properties and application

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Abstract. The theoretical and practical aspects of the synthesis of organic and inorganic macroporous monolithic systems is analyzed. Their structures depend on phase separation during polymerization or polycondensation. The formation of the hierarchic structures based on such systems, modification of the pore surface and application of macroporous monolithic materials are considered. The bibliography includes 115 references.

I. Introduction

Different classifications of porous systems according to their pore size are known. A convenient classification based of the capillary condensation phenomenon was proposed by Dubinin,[1] it has officially been accepted and recommended by IUPAC in a slightly altered form.[2] According to this classification, the pores in which the capillary condensation occurs (and can be measured) are called mesopores. All pores larger in size belong to macropores, while smaller, to micropores. Actually spongy and corpuscular systems with pore widths exceeding 50 nm belong to macropores. Micropore widths do not exceed 2 and mesopores possess widths in the range of 2 to 50 nm.

For the discussion of the membrane mass transfer, another classification is used: the membranes with the pore diameter < 500 nm are defined as microporous; those with the pore diameter > 500 nm, to macroporous. Such subdivision is due to the transfer mechanism of the molecules: if the pore diameter is much smaller than the mean free path of molecules, the Knudsen molecular flow is realized where the probability of collision between the molecules is smaller than that of their collision with the pore wall with consequent bouncing off it. In the macropores, the transfer occurs as the viscous flow of the substance.

Thus, the lower limit of the macropore size is governed by the area application of porous systems (adsorption, filtration, catalysis), while the upper limit is not defined at all. Macroporous materials include ceramic and metallic units obtained by sintering of powders, highly porous cellular materials, products of self-propagating high-temperature synthesis where the pore sizes can attain 100 μm and more. The field of application of open-cell materials with pores of large sizes includes filtration of liquids and gases, catalytic processes that occur in the outerdiffusion region, *i.e.* processes where the surface area of pore walls does not matter that much. It should be noted that many of the materials mentioned are monolithic, *i.e.*, are produced and utilized as a single block.

The monolithic design improves functional properties over a material, significantly facilitates the control of structural parameters and ensures the ease of substitution of used blocks. The high permeability (towards gases and liquids) of monolithic macroporous materials attracts interest in them from the fields where traditionally bulk or compacted micro- and mesoporous materials with high specific surface area are used, *viz*., chromatography, ion exchange, catalysis, sensor design. It is assumed that macropores should play the role of transport channels for compounds subject to reaction, separation or detection, while sorption processes or chemical reactions proceed on pore walls. Here, permeability, pore content and the specific surface area of a material are especially important. Sintered blocks consisting of fairly closely packed particles possess low pore content, that is why the compromise between permeability and specific surface area cannot be achieved in this case. At the same time, the use of such blocks in microreactors[3] shows substantial advantages of the monolithic design.

Materials with structures formed as a result of microphase separation upon polymerization or polycondensation have high permeability and rather high specific surface area. Significant advantage of such materials is the high pore content, which can attain 80% and even more. Historically, ion-exchange resins were the first materials of this type,

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their creation dates back to the middle of the 20th century. Their inner structure consists of randomly packed agglomerates separated by continuous channels. The size of spherical particles of an ion-exchange resin is several microns, the pore diameter is 10 – 120 nm. Compared to gel ion-exchange matrices, they are characterized by higher exchange rates, higher sorption capacity and insignificant size change upon changes in ionic strength of solution. These materials are block, rather than monolithic by nature, as they are prepared as separate particles. Lately, significant number of publications have appeared devoted to the synthesis of polymeric macroporous monolithic materials that are used in different fields of chromatography.[4] The main theoretical provisions have been formulated and methods have been created that allow changes in, and control over, their structure in a wide range. However, low chemical and thermal stability of polymers slightly limit the area of their application.

Macroporous oxide materials obtained by the sol – gel method are distinguished by high thermostability.[5] The processes of microphase separation in these systems are being intensively studied over the past 15 years. Certain practical results were obtained: by varying the reaction mixture composition, one can create both spongy and corpuscular oxide blocks of large sizes containing macropores with widths from 0.05 to 100 μm. Monolithic materials based on silica, alumina, zirconia and titania have been synthesized, they withstand water vapour and high temperatures.

It should be noted that the processes of phase separation in systems during polymerization and in systems that undergo sol – gel transformation are highly sensitive to slight variations of the conditions of synthesis, which in many cases leads to irreproducibility of the results and wide distribution of pores according to the size. The template synthesis of macroporous systems is free from such drawbacks. The appearance of sol with subsequent formation of gel in this case proceeds in the free pore space of the template. Polymeric microspheres,[6] natural materials[7] and even microcrystals of ice can be used as templates. Materials synthesized with the use of templates possess highly ordered structures, which results in the appearance of new properties and enlarges the field of their application.

For their usage in catalysis and chromatography, the monolithic materials, apart from the high pore content and permeability, should possess high specific surface area. This is attained by the structuring of pore walls at the meso- and microlevels. Such materials are called materials with the hierarchic porosity. Macroporous materials with the micro- and mesoporous walls are obtained by addition of surfactants to the sol – gel system.

For the practical use of monolithic porous materials, it is necessary to add certain functional properties to their inner surface. Thus for the different types of chromatography, the modification involves grafting of different functional groups to the initial surface. The usage of monoliths as catalysts requires the application of an active compound, predominantly in the nanoform, onto the pore walls. Conventional impregnation and precipitation procedures cannot be applied in this case, as they do not ensure uniform distribution of the particles throughout the block of large size. The introduction of particles of an active component into the mixture in the initial stage of polymerization is not advisable, as they can either be encapsulated by the polymer or the oxide or lose their activities upon the thermal treatment (calcination) of the monolith. Significant success can be achieved if the formation of an active component is performed in the bulk of the solution that fills the pores.

II. Polymeric macroporous monoliths

In the 1950 – 60ies, granulated polymeric sorbents with open-cell structure in dry state were obtained using a new method of polymerization.[9, 10] The novelty of this method was that the free-radical copolymerization of two vinylic monomers was performed in the presence of an inert compound that was soluble in their mixture but did not act as a solvent for the copolymer formed. One of the monomers was monofunctional and the second, bifunctional, which resulted in the formation of a three-dimensional net-work structure during the polymerization. The inert solvent played the role of the porogen. After its removal by washing or steam distillation, a network of interpenetrating pores was formed in the polymeric material, which was retained in the dry state. Polymerization was performed in emulsion, so the final product represented separate granules with sizes from 0.1 to 1.5 mm.

Copolymerization of styrene with divinylbenzene (DVB) is the most widely and fully studied process,[10, 11] later the list of monomers was significantly extended. Macroporous polymers based on acrylamide (AA), methacrylic, acrylic and maleic acids, methyl methacrylate, acrylonitrile, and their aromatic derivatives as well as based on hydroxyethyl methacrylate and glycidyl methacrylate (GMA) were obtained. In addition to DVB, dimethacrylates and diacrylamides were mostly used as the cross-linking agents, *i.e.*, as bifunctional monomers and such solvents as toluene, cyclohexanol, DMF, DMSO, neat or mixtures with water and methanol as porogens.[12] At present, macroporous network polymers are applied as a material for the preparation of ion-exchange resins and as selective sorbents;[13] a wide range of such materials is manufactured industrially.

The processes of the formation of porous structures in polymeric macroreticular materials are described in many publications, including several reviews.[12, 14 – 16] It was established that the porous structure of a polymer remaining in the dried material appears as a result of phase separation, which begins in the certain stage of polymerization so that two phases are formed that consist of high- and low-molecular components.

The mechanism of phase separation in the cross-linked polymeric systems is not totally clear yet. It was suggested[12] that the formation of the porous structure resuls from macro- or microsyneresis. In the case of macrosyneresis, gel formation occurs in the system in the initial stage of polymerization, its three-dimensional network includes low-molecular components. Then, as the density of cross-links increases and a critical point is reached, collapse of the gel occurs with the formation of microgel the particles of which are distributed in the dispersion medium containing the pore-forming agent and a mixture of non-consumed monomers. Ensuing polymerization leads to local binding of the microgel particles through the terminal vinyl groups and the surface radical centres. This process is accompanied by a significant shrinkage of the sample. In the last stage of the synthesis, the formation of a heterogeneous gel occurs, which consists of two spatially continuous phases, *viz*., the polymer and the porogen. Removal of the latter creates interpenetrating pores of different size.

Under certain conditions, when the system attains its critical point, the occurrence of microsyneresis can be observed where phase separation results in the formation of a dispersion of the liquid phase in the gel bulk. In contrast to macrosyneresis, the gel is not changed in volume, but becomes turbid due to light scattering on the separate drops of liquid. The subsequent polymerization and cross-linking fix this two-phase structure. Following microsyneresis and removal of the porogen, the polymers are formed that contain spherical pores in the gel phase.

The relative probability of micro- and macrosyneresis depends mostly on the content of the cross-linking agent. Macrosyneresis is typical of the systems formed at high concentration of the bifuctional monomer and characterized by high density of cross-linking. Relaxation of the polymeric molecules in the highly cross-linked system is hindered, thus the gel decomposes. At the low content of the cross-linking agent, the network undergoes complete relaxation and the phase separation proceeds in the form of microsyneresis.

Phase separation in the system can start even before the system has passed the point of the beginning of the gel formation, which is often observed where high-molecular or long-chain compounds are used as porogens. In this case, the phase dispersion enriched in the polymer is formed in the volume of the phase depleted in the polymer. Subsequent polymerization leads to the formation of separate polymeric globules, their aggregation creates the continuous phase of the cross-linked polymer of a corpuscular structure. If the amount of the porogen in the system is above a certain limit, the separated polymeric phase can remain dispersed even after full conversion of the monomers. This mechanism was called[12] χ-induced syneresis (χ is the parameter of interaction between the polymer and the solvent), although it was suggested[17,18] that the phase separation of this type occurs by the mechanism of the spinodal decomposition (see next section). In any case, it is the incompatibility of the segments of the polymeric network and molecules of the porogen that is responsible for the formation of pores.

The overall porosity of the final product, which is expressed in percents or volume ratio, depends on the volume of the porogen added to the system and on the swelling degree of the polymeric material, while the pore size is determined by numerous factors: mechanism of phase separationg, density of cross-linking and, mainly, by the parameter of the thermodynamic affinity of the porogen for the polymer. In the systems prepared in the presence of a thermodynamically 'bad' solvent, larger pores are formed. It should be noted that the polymer formed is not uniform in is composition due to different reactivities of comonomers.

The development of methods of preparation of macroporous polymeric monoliths started[19,20] in connection with the progress in chromatographic methods of separation. It is known that the efficiency of the chromatographic separation on packed columns is limited by the mobility or diffusion of sorbates in the stall zones of the stationary phase, *viz*., in dead-end pores and narrow interparticle regions. In the monolithic porous materials, which have sponge-like structure (the system of interpenetrating spherical pores), the stagnant zones are absent, so the perspective of their application as stationary phases was predicted long before their advent.[21] Concerning materials of corpuscular structure, macropores located in them increase the permeability and reduce the hydrodynamic resistance, which allows significant reduction of the working pressure. At the same time, high separation efficiency is retained at high flow rates. The application of the monolithic stationary phases in the chromatographic separation is described in numerous papers and several recent reviews.[4,22–27] Monolithic columns based on polymethacrylate, polystyrene and polyacrylamide are manufactured currently by such companies as BIA Separations, Bio-Rad, Dionex, LC Packings. Columns have disc-like and cylindrical forms, the pore size is equal to 1 – 3 μm.

The method of preparation of the monolithic polymeric specimens differs from that of the granular sorbents in that the preparation of emulsion of the polymerizing components is not required. Monomers and a porogen are mixed, and bulk polymerization is carried out. The mechanisms of phase separation are analogous to those for the emulsion polymerization, and the general tendencies are preserved. First successful studies were connected with the synthesis of porous monoliths based on styrene – DVB copolymers,[28–30] later the list of monomers was significantly extended.

However, the problem that is not solved so far is the low reproducibility of the parameters of the porous structure throughout the monolith. The polymerization reaction is exothermic, and hindered heat removal typical of the blocks of large size creates zones of local overheating closer to the centre of the block, which causes widening of pore size distribution. It was shown[31] that the decisive role in the reproducibility of the porous structure is played by the thorough control of the kinetics of polymerization processes and phase separation.

The influence of the composition of the polymerizing mixture, the type of the porogen and temperature on the parameters of the porous structure of GMA and ethylene glycol dimethacrylate (EDMA) copolymer obtained in the presence of cyclohexanol, 1-dodecanol and sodium carbonate has been investigated.[32] It was shown that the increase in the content of cyclohexanol from 40% to 80% leads to the increase in the pore size from 115 to 875 nm, pore content from 35% to 87% and to the decrease in the specific surface area from 26 to 2 $m^2\ g^{-1}$. The increase in the polymerization temperature from 55 to 70 °C leads to the twofold decrease in the pore size, decrease in pore content and increase in the specific surface area from 7 up to 24 $m^2\ g^{-1}$. Therefore, thorough temperature control is the main task in the synthesis of monolithic porous polymeric materials.

An original method for the synthesis of porous polyacrylamide has been suggested.[33] Polymerization of a mixture of acrylamide, *N,N'*-methylenebis(acrylamide) and allyl glycidyl ether began after it had been cooled stepwise first down to 6 °C and then to −12 °C. The temperature control was performed with a probe introduced into the polymerizing mixture. The ice microcrystals formed played the role of a template.

Cryogels obtained at reduced temperatures contain interconnected spherical pores of size 1 – 100 μm (Fig. 1) are durable and elastic.[34–36] Columns based on monolithic cryogels were tested in the separation of biomolecules, bioobjects (cells, bacteria, blood components), immobilization of bacteriophages and exhibited high efficiency. Elas-

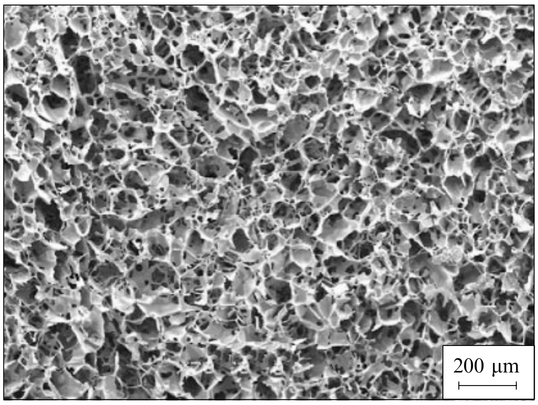

Figure 1. Microphotography of polyacrylamide cryogel.[33]

ticity of the cryogels allows varying the parameters of their porous structures by single-axis compression to 50% of their initial length, which results in a decrease in void sizes and, hence, to a decrease in the number of fractions and to the increase in the concentration of the elute components.

A method of synthesis of a polymeric monolithic material is described[37] in which the phase separation occurs in the form of microsyneresis. The method consists in the radical copolymerization of methyl methacrylate with potassium methacrylate in the presence of a porogen, *viz.*, poly(ethylene glycol). Washing out of the latter leads to the formation of a system of spherical pores with the size of about 0.5 μm localized in the gel phase and filled with the solvent (Fig. 2). The copolymer does not contain any chemical cross-links, the gel network is formed by the intermolecular engagement and the system of hydrogen bonds.[38] The presence of carboxyl groups in the polymer confers ion-exchange properties. The structure of this type of polymers containing water-filled pores in the polyelectrolyte gel was named 'Swiss cheese'. Mathematical modelling of sorption of salts by such gels showed that due to the Donnan effect the concentration of salts in pores is significantly higher than their concentration in the gel phase, the extent of adsorption increases with the increasing the pore size and concentration. Such materials are suitable for the application as microreactors in nanotechnology.[39]

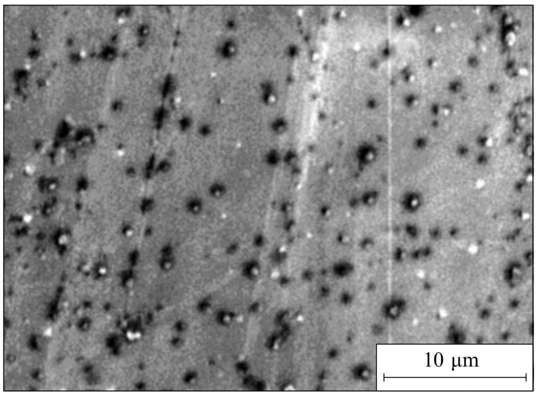

Figure 2. Microphotography of the surface of a porous polymer with the structure of the 'Swiss cheese' type.[37]

III. Oxide macroporous monoliths

Compared to polymers, inorganic oxide materials are characterized by higher strengths, thermal and chemical stabilities, which essentially widens the area of their application. High-purity and homogenous oxide materials can be prepared using the sol–gel synthesis, which allows the control of the structure of products at all stages of the process; this technology is under constant development and improvement.[40–43] Sol–gel processes are carried out in aqueous salt solutions and in alcoholic solutions of metal alkoxides. With alkoxides, the final material turns out to be more pure and homogeneous and does not contain ions of alkali metals.

Sol–gel transition in a system is caused by two parallel reactions, *viz.*, hydrolysis and polycondensation. As a result of hydrolysis of alkoxysilanes, the alkoxide group is replaced by the hydroxyl group. Hydrolysis proceeds more rapidly and is completed in the presence of catalysts; these are inorganic acids, aqueous ammonia, acetic acid, amines, alkali metal fluorides, titanium and vanadium alkoxides. Inorganic acids are more effective as the hydrolysis catalysts than bases.[40–43]

In the course of the polycondensation, M–O–M (M is metal) bonds are formed as well as by-products, water or an alcohol. Polycondensation leads to the growth of metal oxide oligomers, which ultimately form the gel structure. After drying and thermal treatment of the gel, it is possible to obtain amorphous and crystal oxide materials in the form of films, fibres or powders, which is another advantage of this method of synthesis. The peculiarity of the sol–gel method is the formation of nanopores filled with liquid in the stage of gel formation. Therefore, bulky samples of gels crack during drying under the influence of the capillary pressure forces and it is necessary to carry out this operation under supercritical conditions for the formation of monolithic units. This affords porous materials, which are called aerogels, the porosity of which can reach 90%.

The idea to apply sol–gel technology for the preparation of macroporous oxide materials appeared in the beginning of the 1990s. The first publications of a group of Japanese scientists[5,44] were dedicated to the synthesis of macroporous silica. The problems that emerged in the subsequent attempts to synthesize macroporous monoliths based on zirconia and titania were connected with that hydrolysis and polycondensation of titanium and zirconium isopropoxides proceed with high rates. As a result, the process of gel formation completes very quickly and the phase separation in the system proceeds by the mechanism of nucleation and growth, which results in the appearance of the oxide dispersions. At present, the methods of synthesis of macroporous bulk materials based on titania, alumina and zirconia have been developed[45,46] in which n-propoxides of the said metals are used; for these compounds, the processes of gel formation at high pH take several hours.

Consecutive stages of the synthesis of macroporous monoliths and processes occurring in each stage can be examined by the example of silicon alkoxides.[47] The most popular silicon-containing precursors are tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), the former being more reactive. Hydrolysis of alkoxides is carried out in the presence of a solvent (usually water), a catalyst and additives such as water-soluble polymers. Silicon alkoxides are insoluble in water, therefore, in the initial stage of mixing the solution can be turbid, but becomes transparent with evolution of alcohols upon hydrolysis. As the heat generated during hydrolysis essentially influences the final morphology of the gel, hydrolysis is usually carried out in an ice bath. The polycondensation that proceeds together with hydrolysis leads to the formation of siloxane oligomers, which contain in addition to the $\equiv Si-O-Si\equiv$ groups also certain amount of unhydrolyzed $\equiv Si-OR$ groups as well as $\equiv Si-OH$ groups.

Following appearance of a homogenous solution, the sample is placed into a hermetic vessel in which gel formation and its ageing proceeds at the temperature in the range of 40 to 80 °C. The open-pore structure is formed following completion of phase separation in the system containing alkoxide oligomers, solvent and porogen, which is a water-soluble polymer in majority of cases.

Synthesis of monolithic macroporous samples requires that the system formed upon phase separation, contains two spatially continuous phases, *viz*., the gel and the porogen. It is in this case that, after removal of the latter, the formation of open macropores is possible that penetrate the whole bulk of the monolith. Therefore, the investigation into processes of phase separation in the course of sol–gel synthesis is an especially challenging task. The change in the free energy of a binary system containing at least one type of polymeric molecules can be described by the Flory–Huggins equation:

$$\Delta G = RT\left(\frac{\Phi_1}{P_1}\ln\Phi_1 + \frac{\Phi_2}{P_2}\ln\Phi_2 + \chi_{12}\Phi_1\Phi_2\right),$$

where Φ_i and P_i ($i = 1, 2$) are, respectively, volume ratio and the degree of polymerization of each component, χ_{12} is the parameter of the interaction between the components. The first two components in brackets express the entropy contribution into the free energy value, while the last one, the enthalpy contribution. With the decrease in the absolute value of the negative entropy component, the system is destabilized, *i.e*., the increase in the degree of polymerization of any of the components makes the mixture less compatible. The contribution of the enthalpy component also depends on the molecular mass of the inorganic polymer, since the amount of hydroxyl groups that effectively interact with molecules of water or a porogen decreases as a result of polycondensation. In other words, the starting single-phase solution containing the polymerizing component becomes less stable with the increase in the molecular mass of the latter, which results in microphase separation.

The process of polycondensation leading to a decrease in the mobility of monomer molecules upon the formation of chemical bonds between them is defined[47] as 'chemical freezing' similarly to the processes proceeding with the decrease in temperature in the chemically inert systems. This fact allows the use, in the sol–gel systems, of the classical thermodynamic approach developed by Gibbs and employed for the investigation of microphase separation in the solidifying polymer–oligomer systems.[18]

The plot of the free energy *vs*. concentration $G(\Phi)$ contains inflexion points where the second derivative changes the sign. In the case where $\partial^2 G/\partial\Phi^2 > 0$, the diffusion flow of components are directed towards the reduction of fluctuations of the compositions, while at $\partial^2 G/\partial\Phi^2 < 0$, the inversion of the diffusion flow occurs (or the so-called 'ascending diffusion' appears). The intensity of the fluctuations is increased, the system, being single-phase, becomes unstable and should spontaneously decompose into the regions of the equilibrium composition. The region of instability of the single-phase system is limited on the phase diagram with a curve, which is called spinodal (Fig. 3). From the 'outer' side, the spinodal adjoins the region of metastable states limited by the binodal where the first derivative $\partial G/\partial\Phi$ has a zero value. On the Y-axis, the quantity is laid that is equivalent to the temperature and reciprocal to the molecular mass of the siloxane oligomers.

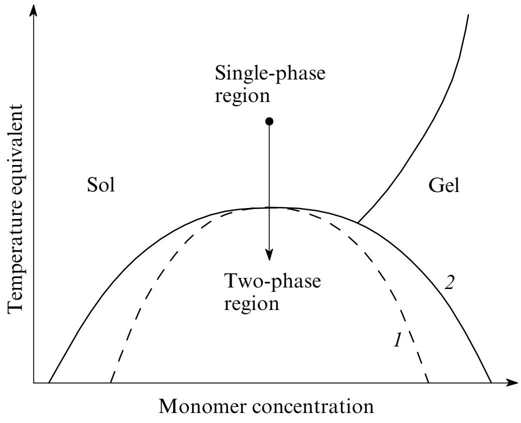

Figure 3. Phase diagram of the gel-forming system.[47]
(*1*) Spinodal, (*2*) binodal.[47]

In the region between the binodal and the spinodal, the diffuse flows of components in the system are directed towards the reduction in the fluctuation of compositions. At the same time, the presence of the energetically unfavorable effect of the formation of the interface leads to the system unstability only in respect of the fluctuations that are larger than the critical value, while fluctuations themselves are close in the composition to the new phase. Such fluctuations are called critical nuclei. The appearing critical nuclei increase in size and the phase separation proceeds by the mechanism of the nucleation and growth. Sol–gel systems with the phase separation according to this mechanism are dispersed in one of the components, which makes impossible the production of the macroporous blocks and monoliths based on them.

In the vicinity of the critical point of the two-phase equilibrium, the region of the metastable states narrows merging to a point. This creates favourable prerequisites for the attainment of unstable states of the system using the near-critical transition through the binodal and the spinodal, which is marked with an arrow in Fig. 3. In the unstable state, the system quickly looses spatial homogeneity and during relaxation acquires particular, modular structure. Under spinodal decomposition, the evolution is understood due to the thermodynamic instability of a continuous heterogeneous structure, similar to that shown in Fig. 4.[47] The spinodal decomposition occurs in the region of high concentrations of both components. The indicator of the phase separation by the spinodal mechanism is the appearance of the diffraction maxima in the SAXS spectrum. The cross-section size of the individual domains in the initial stage of the spinodal decomposition depends on the rate of the transition of the system into the unstable state and does not exceed 100 nm. Subsequently, the heterogene-

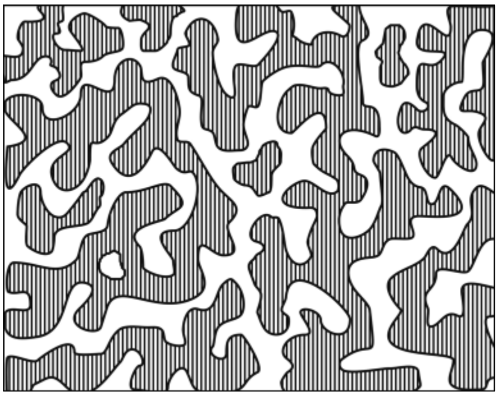

Figure 4. The view of structure formed according to the mechanism of the spinodal decomposition.[47]

ities can enlarge without losing the spatial continuity and reaching the size of 1 μm and even more or decompose into smaller entities. Investigations into the kinetics of the spinodal decomposition started by Cahn and Hilliard[48] allow tracing in time the process of the appearance, enrichment and, in some cases, coalescence of the microregions of a certain structure.

The spinodal decomposition in the system containing siloxane oligomers results in the formation of two spatially continuous phases, one of which is enriched, while the second is depleted, in the oligomers. Together with the phase separation, the formation of the gel cross-linking occurs in the system, which results in the reduction of the mobility of the components. This allows constraining the bicontinuous structure and ensures the possibility of obtaining on its basis open-pore monolithic materials. The resulting morphology of the sample depends on the kinetics of the coalescence of the microregions that were formed in the course of the spinodal decomposition and kinetics of the sol–gel transition. The structural parameters of porous monoliths during the synthesis can be monitored using X-ray small angle scattering, scanning electron microscopy and laser scanning confocal microscopy.[49–51]

Gel maturation occurs in a sealed vessel at the temperature of gelation. In the course of the ageing, hydrolysis and polycondensation that occur more slowly in the gel continue, which results in the appearance of additional cross-links in the gel network. The time required for the gel to ageing is usually several times larger than the time of gelation and the indication of its completion is usually shrinkage of the sample and liberation of the solvent from the bulk (syneresis). The wet gel should be aged enough before the start of the process of the solvent substitution to obtain pores with a narrow pore size distribution.

The next stage of the formation of the macroporous blocks is the solvent exchange, which is carried out when the gel is sufficiently mature, but is still wet. The main point of this process is the immersion of the gel into a solvent (the so-called external) that differs from the one employed in the synthesis. Aqueous ammonia is often used as the external solvent since the alkaline medium increases the rate of the polycondensation reaction, durability and modification of the meso- and microporous gel structures. The modification of the gel structure under the influence of the external solvent in which amorphous silica has a considerable solubility is governed by the process of solution–recrystallization of the fractal surface of the gel network. So, the increase in the pH value of the external solvent is the most acceptable way of the increase in the mean pore size with the preservation of the pore size distribution width.[52]

Instead of exchange of the solvent for aqueous ammonia, hydrothermal treatment is sometimes used. Urea is added in the initial stage of the sol–gel synthesis with subsequent (after ageing) heating of samples to the temperature above 80 °C where urea decomposes yielding ammonia. In the course of the hydrothermal treatment at the elevated temperature and high pH values, mass transfer and silting of sites of the gel particles contact occur, which makes the structure more stable and allows avoiding cracking of the samples during drying under ordinary conditions.

Drying of the wet gel samples is performed in an air circulation oven, the volatile components being slowly evaporated. The required temperature ranges from 40 to 80 °C depending on the solvent used. In the preparation of the monolithic solid samples, the drying is the critical stage. The Young–Laplace equation expresses the dependence of the capillary pressure (P) in a cylindrical pore on the surface tension (γ) at the liquid–vapour interface, the contact angle (θ) and pore radius (r):

$$P = \frac{2\gamma\cos\theta}{r}.$$

In small pores, the capillary pressure is high, so drying of nanoporous gels is carried out under supercritical conditions where the liquid–vapour interface in absent. The capillary pressure in macropores is much smaller, and on slow evaporation of the solvent macroporous gels withstand drying under ambient conditions. It should be noted that the violation of the sample integrity during drying is due to the appearance of the pressure gradient rather than to the capillary pressure, and the increase in the linear size of the gel increases significantly the risk of cracking. High-molecular porogens, remaining in the pores even after the solvent exchange, ensure additional gel elasticity and favour the preservation of its integrity. The linear shrinkage of samples during ageing and drying ranges from 50% to 70%. The pore sizes decrease proportionally.

Thermal treatment is the final stage of the monolith preparation, which ensures decomposition of organic components. Heating of the sample to the temperature $\leqslant 1000$ °C and its cooling are performed at a rate of $\leqslant 100$ deg h^{-1}. In the thermal treatment, the final modification of the structure occurs besides removal of organic components. Heating of samples to the temperature of 600 °C causes collapse of nanopores and reduction in the mesopore share.[53] Upon heating above 1000 °C, mesopores disappear and porous glasses are obtained.

For the sol–gel technology, in contrast to the technology of macroporous polymers, there are no general dependences that describe the influence of the concentration of a component and conditions of synthesis on the resulting gel structure. Since hydrolysis and polycondensation are caused by acid-base interactions in the system, the porogen is not the inert compound in the full sense of the word: it can exchange ions with the solution, which is typical, for example, of sodium polystyrenesulfonate or polyacrylic acid, and also adsorb on the surface of the siloxane oligomers, like poly(ethylene oxide) (PEO), or undergo hydrolysis, like formamide. That is why, the concentration dependences of the macropore sizes contain maxima related to the variation of the structural characteristics of the monolith, formation of spherical particles in macropores, *etc.* By now, the most investigated systems are those in which the porogen is PEO with molecular mass (MM) 10 000 – 100 000. It was shown,[54] that for PEO with MM = 35 000 the increase in the molar ratio PEO : Si in the system from 0.5 to 0.7 leads to the decrease in the pore size from 10 to 0.2 μm. The increase in MM of the polymer leads to the decrease in the pore size.

Macroporous monoliths synthesized by the sol – gel process have bimodal pore size distribution and contain macropores with sizes 1 – 5 μm and mesopores with sizes ~10 nm. The overall porosity can come up to 70%. Chromatographic columns in the form of rod-like monoliths based on macroporous silica prepared by the Nakanishi and Soga method [5, 44] covered with thermocontractable polymer are manufactured by Merck under the trademark Chromolith.[55–57]

IV. Monoliths with hierarchical porosity

The improved transport properties of the macroporous monoliths are due to the presence of the pores of large sizes. At the same time, for their practical application high specific surface is required, as it is on the surface that adsorption and desorption as well as chemical reactions occur. One of the ways to increase the specific surface of the macroporous monolithic materials is the modification of the texture, *viz.*, creation of mesopores on the surface and in the volume of the oxide framework. Materials with the bimodal pore size distribution are also called materials with hierarchical porosity.[58] The lower limit is represented by mesopores, while the upper, by macropores. The specific surface area of such materials can reach 300 $m^2 g^{-1}$ and even more.

As was mentioned above, the gel network of the oxide oligomers obtained by the sol – gel method contains nanopores filled with a solvent. One of the methods for the texture modification is the holding of the aged gel in the alkaline medium at elevated temperature. The parts of the framework with small positive curvature are dissolved with subsequent oxide precipitation on the regions with small negative curvature. As a result of the mass transfer, nanopores with widths of 1 – 2 nm are transformed into mesopores with the size up to 15 nm. The processes of the formation of mesopores in the oxide materials do not involve macropores, until dissolution of the oxide framework becomes so substantial that it would lead to the deformation of the entire monolithic material. It is evident, that the modification of the texture of the polymeric monolithic material by this method is impossible as atoms in the polymeric molecules are bound by strong covalent bonds. Mesopores that are formed as a result of the texture modification have a rather narrow size distribution, but they are not ordered.

The creation of the mesoporous materials with regular structure was realized in the 1990s, when researchers of the Mobile Research and Development Corporation obtained first ordered mesoporous materials MCM-41, MCM-48, MCM-50.[59, 60] The synthesis of such materials was performed by the sol – gel method in the presence of micellar solutions of surfactants. Some time later, papers appeared devoted to the synthesis of macroporous monolithic materials containing regular mesopores.[61] Non-ionogenic surfactants were used as porogens. It is possible to combine the formation of the macroporous structure with supramolecular templating and precipitation, as they both include polymerization-induced phase separation.[62]

The synthesis of hierarchical monolithic materials [61] consists of the application of polyoxyethylene nonyl phenyl ethers containing 10 to 70 hydrophilic oxyethylene units as non-ionic surfactants. In the case of surfactants with long oxyethylene chains, the hierarchical structure ordered at the mesolevel is formed in the narrow concentration range of the three-component system containing a porogen, water and TMOS. In other regions of the phase diagram, only mesoporous materials, gel dispersions and systems that decompose into two microphases formed. Surfactants with long hydrophilic chains strongly adsorb on the surface of silica even at low concentrations. Following adsorption of the first monolayer, the next layer is adsorbed on the surface that has become hydrophobic, again making it hydrophilic. Thus, the inversion of hydrophobicty is observed. Molecules of surfactants with short chains are weakly adsorbed on the surface of SiO_2, no inversion of the hydrophobicity occurs, so the monoliths with hierarchical structure can be synthesized in the wide interval of concentrations of the starting reagents. The following regularities have been established: 1) with the increase in the number of the oxyethylene units of the surfactant, the fraction of micropores in the material is increased; 2) the earlier the phase separation occurred in respect of gelation, the larger is the size of macropores. The stage of the solvent exchange for 1 M HNO_3 or 1 M NH_4OH was carried out after gel ageing; the treatment with nitric acid led to the decrease in the overall volume of micropores, and ageing in the ammonia medium, to their complete disappearance.

Triblock-copolymers Pluronic P123 and F127 were used as porogens.[63] The oxide networks of the macroporous monoliths synthesized in their presence included ordered mesopores of different forms. The introduction of cetyltrimethylammonium bromide into the system containing TEOS and PEO allowed preparation of macroporous monoliths in which the walls are structured as in MCM-41.[64]

V. Modification of the monolith surface

A wide application field of the monolithic porous materials necessitates the modification of their surfaces with various functional groups and active sites in order to obtain the desired properties. Sometimes, the modification of the monolith surface can be performed by introducing components with certain functional groups into the initial mixture. However, if polymers are concerned, due to the difference in the reactivities between the functionalized monomers and other monomers present in the mixture, the functional groups can become inaccessible after polymerization, *i.e.*, encapsulated in the network of the block.[12] Therefore, in most cases modification is carried out by grafting compounds containing functional groups to the surface of the prepared monoliths. Particulate sorbents modified in this way have widely been used in chromatography and sensor design since a long time ago. The processes of their preparation consisting of attaching a compound to be grafted through surface anchor groups with formation of chemical bonds with the functional group [65] are applicable to the monolithic materials.

Due to the hydrophobic nature of the surface of the non-modified monoliths, they can successfully be used for the reversed-phase chromatography, but even in this case the grafting of C_{18}-groups to the surface of a monolith prepared by copolymerization of GMA and EDMA increases the protein separation efficiency.[66] Modification of the polymeric monoliths can be performed through epoxy-,[67] chloromethyl[68] or azlactone[69] groups. Another popular method consists of the GMA epoxide ring-opening grafting, this being one of the co-monomers. Using this method, stationary phases for the ion-exchange, pH-gradient and affinity chromatography were prepared. The grafting of the amino groups onto the surface of the poly(GMA/DVB) monolith was effected by the epoxide ring-opening in the reaction with diethylamine.[70] Consecutive treatment of the same monolith with diethylamine and diethyl sulfate resulted in grafting of the quaternary ammonium groups to the surface thus converting it in a strong ion-exchanger.[71] Weak cation-exchange resins were prepared on the basis of the monolith of poly(GMA/EDMA) by consecutive treatment with diethylamine and monochloroacetic acid.[72]

The procedure for the preparation of a versatile modified monolith was described,[73] its surface can easily be functionalized by different groups for specific applications. The transformation of the pendent 2,3-epoxypropyl groups of the GMA comonomer in a GMA/EDMA polymer in 2-mercapto-2-hydroxypropyl groups was effected by treatment with sodium hydrogensulfide as a nucleophilic agent. Reactive thiol groups on the surface of the monolith can subsequently be used as an anchor for the attachment of other ligands by different chemical reactions, such as radical addition, grafting polymerization, nucleophilic substitution.

Photopolymerization can be also used as a way of the surface functionalization. Thus benzophenone was used as a sensitizer for the attachment of 2-acrylamido-2-methylpropane-1-sulfonic acid and 4,4-dimethyl-2-vinylazlactone to the surface of poly(butyl methacrylate/EDMA) under UV irradiation.[74]

Commercially available silica-based monoliths prepared by hydrolysis and polycondensation of TMOS and TEOS are devoid of functional groups on their surface except for the silanol groups. In numerous papers, the methods of their modification are described, which involve the introduction of different substituted silicon alkoxides into the reaction mixture in the stage of synthesis, since for the oxide materials, compared to the polymeric, the probability of encapsulation of the functional groups is significantly smaller. Studies on the methods for the creation of the hybrid materials containing silicon – carbon bond are the most popular. Organosubstituted silanes, such as octadecyltrimethoxysilane,[75] phenyltriethoxysilane, octyltriethoxysilane,[76, 77] methyltrimethoxysilane,[78] giving the surface hydrophobic properties, are introduced into reaction mixtures. Weak anion-exchange properties of the surface of the oxide monoliths are conferred by such compounds as 3-aminopropyltriethoxysilane[79] and other aminosilanes. Sometimes organosubstituted silanes introduced into the reaction mixture contain anchor groups necessary for subsequent functionalization of the monolith surface. For example, methacrylic anchor groups are introduced by the co-condensation of alkoxysilanes with *N*-(3-triethoxysilylpropyl)methacrylamide[80, 81] or 3-methacryloyloxypropyltriethoxysilane.[82] In the course of the subsequent functionalization, these groups allow grafting to the surface of the monolith of polyacrylamide,[80] polyacrylic acid[81] and poly(methyl methacrylate).[82] Monolithic columns functionalized by this method were employed for the separation of polar compounds, *e.g.*, proteins and nucleic acids, and were used as cation- and anion-exchange resins.

The surface silanol groups of the monolith can act themself as the anchors. They participate in the grafting of octadecyldimethyl-*N*,*N*-diethylaminosilane[83 – 85] to the surface of the monolith for the preparation of the so-called ODS-monoliths (octadecyl-silica monoliths), widely used in the reversed-phase chromatography.[86] Different methods of modification of silica monoliths for their application in different areas of chromatography are reviewed in detail.[22]

It should be noted that the uniformity of the distribution of a modifier in packed columns is provided by vigorous stirring of the carrier during its application, fast introduction of the reactants into the solution and random distribution of particles in the column. During modification of the monolithic material, no stirring is carried out, and the reactants penetrate the pores of the monolith over a rather long period of time, which can lead to the appearance of the concentration gradient of the modifier along the monolith block. However, even such monolithic materials can successfully be used in the gradient chromatography.[87]

The use of porous monoliths in the catalytic reactors requires the deposition of the active component of the catalyst onto the walls of the macropores. The immobilization of coordination compounds of transition metals on the surface of solid carriers allows one to obtain heterogeneous metal complex catalysts (HMC) active in the catalytic transformations of different types of organic and inorganic compounds. To date, the number of papers devoted to the synthesis and application of HMC based on particulate carriers is about several thousands. It should be expected that the results obtained will be used for the synthesis and investigation of properties of HMC based on the monolithic systems. Indeed, the possibility of the application of the porous block based on a GMA – EDMA copolymer in a capillary flow reactor was shown.[88] The length of the monolith with pores of 1 μm was equal to 20 cm, its diameter — 250 μm. Upon completion of the synthesis of the monolith, a palladium phenanthroline complex was attached to its surface. The capillaries obtained were assayed in the Suzuki – Miyaura reaction (aldol condensation); high yields of the products were obtained while the catalyst possessed good stability.

The supported metal catalysts consisting of separate granules with clusters and nanoparticles of metals and alloys as the active components are widely used in different chemical processes. The deposition of an active component as nanosized particles onto the surface of oxide carriers (as well as metal carbides and nitrides, porous carbon materials, *etc.*) allows a substantial increase in the reactivities of the surface active sites as compared to the polycrystalline systems due to the dramatic changes in the material properties upon reduction of the particles size down to the nanometer scale.

As concerns monolithic catalytic systems (monolithic reactors), the first successful attempts of the creation of commercial samples of this type of supported catalyst, possessing high permeability towards gases for the catalytic converters of exhaust gases date back to the beginning of the 1970s.[89] Since then, the interest in the application of monolithic materials has steadily grown in the environmental catalysis: in the processes of ozone decomposition; oxidation of carbon monoxide and hydrocarbons in exhaust gases; selective reduction of nitrogen oxides; decomposition of volatile organic pollutants in the industrial wastes of chemical plants and municipal systems, *etc*. One can mention a series of catalytic technologies in progress that use monolithic reactors, including hydrogen generation in fuel cells, vapour reforming of hydrocarbons, selective oxidation of carbon monoxide at low temperatures, ammonia oxidation into nitrogen oxides, the Fischer – Tropsch synthesis, *etc*. Different types of monoliths are documented [90] that are used in the catalytic processes: most frequently used are systems with the channel diameter of 1 to 5 mm, however the possibility of the application of monolithic reactors with ultrafine channels (down to 20 μm) is also considered.[91] Oxide monolithic materials with porous structure formed during the synthesis as a result of phase separation have high potential for the application in different catalytic processes, while the problem of the deposition of the catalytically active components onto the macropore walls as finely dispersed phase is also rather topical.

The technologies of the deposition of nanosize modifiers onto the outer surface of particulate carriers of different nature are numerous and rather thoroughly investigated. Some of them can be equally applied for the monolithic systems virtually unchanged. Thus the method suggested for the immobilization of gold nanoparticles on the surface of thin films,[92] microspheres [93] and mesoporous granules of silica [94] can be used for the deposition of these nanoparticles onto the pore surfaces of the monolithic materials. The process includes [95] the stage of the functionalization of the silica surface with amino groups by treating it with aminosilanes, the synthesis of gold nanoparticles in an aqueous medium according to the conventional citrate method [96] and the introduction of the gold citrate sol into the medium containing the functionalized oxide. The Coulomb forces ensure the irreversible adsorption of the negatively charged gold nanoparticles on the positively charged aminated surface. A variant of this method consists of the *in situ* reduction of tetrachloroauric acid with citrate in the medium containing silica microspheres with functionalized surface,[97] which allows enhancement of the uniformity and degree of coverage of the carrier surface with gold nanoparticles.[93]

The latter method is characterized by the *in situ* formation of the metal nanoparticles, *i.e*., directly in the presence of a carrier. Conventional methods of this type, otherwise called 'impregnating', consist of the impregnation of particulate carriers with metal salt solutions, drying and subsequent reduction (preferably in the flow of hydrogen). For them, the effects of the active component redistribution in the stages of drying and thermal treatment are typical.[98, 99] It is clear that the selection of the monolithic material as the carrier aggravates these effects. The sorption immobilization of metal ions on the pore walls with subsequent reduction could prevent their redistribution in the bulk. However, the application of such techniques for the synthesis of monolithic macroporous nanocomposites faces the problem of the uniform distribution of nanoparticles in the volume of the pore space. Drying of the monolithic block takes a rather long time, during which the fixed ions can undergo desorption and redistribution.

The drying step of the monolith can be excluded as in the case of the deposition – precipitation procedure.[100] According to this method, the precipitation and reduction reactions are carried out in the solution with vigorous stirring, the metal ions and the precipitant (reductant) are successively introduced into the solution. However, if the reaction is carried out in the pores of a rather bulky monolith, fast successive introduction of the reactants is not possible. The metal ions introduced into the pore space create the diffuse flow towards the reaction front upon introduction of the reductant into the system. The result of such processes is the enrichment in the active component of the monolith layers close to the surface and, respectively, its almost complete absence in the centre of the block. Thus, the processes of the formation of finely dispersed particles of the new phase within macropores of a monolithic material are hindered by several factors. Therefore, papers on this topic are not numerous, investigations are in the infancy, but first positive results have already been obtained.

A method has been described [101, 102] that allows formation of silver nanoparticles in the pores of silica aerogel by stepwise introduction of silver ions and reductant (hydrogen) into the porous system. The principal novelty of the suggested approach consists of carrying out the reduction reaction in a thin film of a silver phosphate melt, which is formed on the pore surface as a result of strong adhesion to the monolith surface containing a great number of silanol groups. Silver ions in the film are uniformly distributed over the monolith volume while fast introduction of the gaseous reductant to the high-permeability system prevents their redistribution in the course of the reduction. Polyphosphates formed upon calcination of the composite sample are effective stabilizers for the silver nanoparticles formed in the block, their sizes do not exceed 10 nm.

Monolithic materials prepared according to this method were split into separate granules and tested in the reaction of partial oxidation of ethylene glycol. Their efficacy exceeds that of the bulk polycrystalline silver.[101]

At present, a number of approaches has been developed that ensure the uniform distribution of metal nanoparticles synthesized in solution that fills the pores of the monolithic material. The general principle of this method [103] consists of that the processes of the introduction of the reactants into the pores and metal ion reduction are time-separated. A procedure for the formation of platinum nanoparticles inside the macropores of the bulk acrylic polymer with the structure of the 'Swiss cheese' type was described.[104] The synthesis has been carried out in the following way: in the first stage, the platinum ions were introduced into the pores of the monolithic block by sorption from an aqueous solution. In the subsequent stage, the reductant (hydrazine hydrate) was introduced at low temperature as a solution in toluene. This method prevents migration of the platinum ions towards reduction front, which would result in uneven distribution of metal nanoparticles in the bulk of the polymer. Then the sample was quickly heated to 70 °C. The nanocomposites obtained were characterized by even distribution of metal particles, which are concentrated mainly inside the pores and absent in the gel phase. Investigations into their structures revealed an unexpected fact: despite the absence of a component that would hinder the aggregation of the platinum nanoparticles formed in the macropores, the size of the nanoparticles did not exceed 5 nm.

The mechanisms of the formation of metal nanoparticles in nanopores,[105] emulsions [106] and reverse micelles [107] (*i.e.* in nanoreactors where the size of the particle formed is naturally limited by the reactor size or material resources in it [108]) are investigated and described in detail.[109 – 111] The formation of a new phase always begins with the appearance of nuclei of the nanometer size. It is evident that the nanoparticle stabilization is possible in macropores only in the case where they appear as homogeneous species inside the pore and immediately attach to the walls so that they are not involved in the aggregation processes. A similar effect can be achieved in the case of heterogeneous nucleation where the particle have initially been attached to the pore wall. Of importance is the amount of functional groups present on the walls, which can interact with the metal ions and adsorb on the surface of the growing particles. The synthesis of macroporous acrylic polymers containing variable percentage of available carboxyl groups was described.[104] It was found that the reduction in the content of the carboxyl groups in the copolymer from 0.8 to 0.45 mmol g^{-1} increases the platinum particle size formed in the pores of approximately similar sizes from 5 to 50 nm. Apparently, large particles represent aggregates (Fig. 5). The amount of functional groups on the pore surface can influence not only the aggregation processes of the particles formed in it, but also on the number of nuclei of the critical size that are formed due to the appearance of a new phase in the pores.[111]

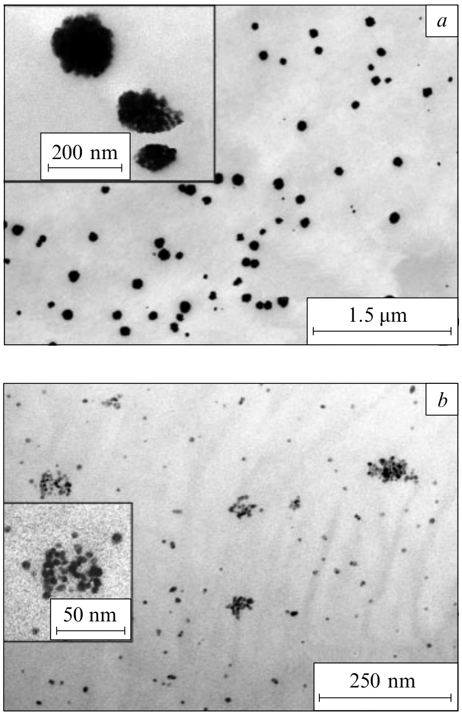

Figure 5. Microphotographs of a porous gel filled with platinum nanoparticles. The carboxylic groups content in the copolymer are 0.45 (*a*) and 0.8 mmol g^{-1} (*b*).[104]

Yet another approach that allows obtaining monolithic materials with metal nanoparticles evenly distributed throughout the bulk consists of simultaneous introduction of a metal salt and a reductant into pores. It was suggested[112] to fill the pores of a polymeric matrix with a solution containing nickel ions and thiourea dioxide (TUDO) as a reductant. In a certain range of concentrations, such solutions are stable for a long time, and at 20 °C the reduction of nickel ions occurs only in the bulk of the polymeric matrix. This fact as well as the dislocation of nickel particles solely on the pore surface point to the heterogeneous mechanism of nucleation. The size of nickel nanoparticles on the pore surface did not exceed 20 nm. An analogous approach based on the use of stable solutions of silver nitrate and different reductants was used for the synthesis of macroporous silica monoliths containing silver nanoparticles.[113]

The possibility of formation of nickel nanoparticles on the inner walls of microreactor in microchannels with diameter of 2 μm was shown.[114] The reduction of nickel ions was carried out in a magnetic field under the influence of γ-irradiation, the nickel particle size was equal to 40–100 nm. The application of γ-irradiation is convenient for the formation of the oxide and polymeric nanocomposites, as it is insignificantly absorbed by the monolith material and evenly influences the entire object. For the blocks of small thickness, UV irradiation is also effective where reduction of photosensitive compounds is concerned. It was shown[37] that the UV irradiation of a porous polyacrylate monolith containing the silver ions results not only in the formation of silver nanoparticles in pores, but also in partial destruction of the polymer. Subsequent thermal treatment of silver–polyacrylate porous nanocomposites leads to complete decomposition of the polymer with the formation of spherical silver agglomerates with sizes of ~100 nm that form a single block. The morphology of the latter is determined by the structural parameters of the polymeric matrix serving as a template.[115]

It should be noted that studies of mechanisms of the formation of a new phase in macropores can ensure the interdisciplinary approach to the investigation into the biomineralization processes.

* * *

Structural parameters and functional properties of macroporous monolithic materials prepared by polymerization and polycondensation can be controlled over a wide interval. The area of their application, initially limited solely by chromatography, constantly widens. It can be expected that monolithic columns, catalytic reactors and sensors will become widespread and partially replace respective particulate materials. Therefore, investigations into the methods of preparation, texture modification and methods of surface functionalization are highly topical.

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