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Optical Sensors Based on Mesoporous Polymers

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Additional information is available at the end of the chapter

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1. Introduction

Porous materials are widely used in such industries as chemical, food industry, petrochemistry, medicine, and environmental protection. Nanoporous materials (NM), characterized by a pore size of 1 to 100 nm, are a great alternative to non-porous materials due to the presence of a number of unique properties. Among NM are microporous materials (e.g. zeolites) and mesoporous materials (e.g., porous polymers, aluminum or silicates). According to IUPAC nomenclature, the definition of "microporous" corresponds to the pore size of 2 nm, the definition of "mesoporous" corresponds to 2-50 nm [1]. By chemical composition NM are divided into aluminum silicates, metals, oxides, silicates, consisting only of carbon and organic polymers. These materials are combined in a high surface area and porosity. NM are used in various fields of chemistry and technology, depending on their chemical composition, pore size and distribution, porosity value.

Promising areas in which mesoporous materials can be successfully used are transparent optical chemical sensors and test methods for the determination of various substances. Sensors and sensing elements on optically transparent polymeric substrates can be more convenient in some cases of analytical practice, as they allow to observe visually the color change [2]. To determine the low concentrations of elements preliminary sorption concentration and subsequent determination by chemical or physico-chemical methods are used. The optical transparency of the sorbent allows to carry out the analytical reactions on sorbent surface and on their basis to develop sorption-photometric and test methods for the determination of substances.

Complexation reactions of organic reagents and a tested ion are the basis of optical chemical sensors for metal cations, they are accompanied by color change of the reaction system. In absorption-based optical sensors, the molecules of organic chromophores are used as a sensing

layer of the substance (receptor), selectively interacting with the analyte [3]. In the case of an luminescence-based optical sensor, the molecules of organic luminophors are receptors. The latter also became common as active medium in dye lasers.

Indicator papers, indicator tablets, powders, solutions in vials may be used as a substrate. There is a number of substrates, such as cellulose, ion-exchange resins, superfine silicas, polyvinyl chloride membranes, etc. where the complexing reagent can be immobilized. The main requirements to the material of the reagent carrier are optical transparency, high sorption rates, ease of synthesis, processability, inertness to the reactants, stability in acidic and alkaline media, high sensitivity to analytes [4].

The natural cellulose polymer is the most widely used as a matrix [5]. A solid carrier is soaked in the reagent solution and then dried. The process can be one-stage or multistage.

The methods of applying reagents to the polyurethane foams are worked out. These methods are based on pre-plasticization of polyurethane foam tablets and the subsequent treatment by small volume of acetone solution of an analytical reagent [6].

Silica gel is a porous, granular silica form synthetically produced from solutions of sodium silicate or silicon tetrachloride, or substituted chlorosilanes / orthosilicates. The active surface of silica gel with a large surface area is of great importance in the adsorption and ion exchange. The modification of the silica gel surface for the analytical reactions is carried out in two separate ways, viz. the organic functionalization, where the modifier is an organic group; and inorganic functionalization where a group fixed on the surface can be an organometallic composite or metal oxide [7].

One of the interesting areas of research is gelatin cured gel applied to the substrate made of a transparent polymer. Gelatin is a polydisperse mixture of polypeptides prepared by alkaline or acid hydrolysis of collagen. Biopolymer has high hydrophilicity, transparency in the visible spectrum, ability to form gels at any weight ratio of water-gelatin. These properties make the systems with immobilized reagents on the basis of such polymer especially attractive for analytical reactions involving water as a solvent [8].

In recent years modified ion-exchange materials prepared by sorption, or chemical grafting of organic reagents using conventional ion exchangers, have found wide application [9]. Such ion exchangers are used for the selective and group concentration of elements, but the most valuable thing is that owing to them, an appropriate element can be simultaneously concentrated and determined quantitatively.

There are a number of shortcomings for the known substrates which limit the prevalence of these materials as the base of optical chemical sensors. Cellulose is non-transparent, has low resistance to aggressive environments, weak physical and mechanical properties. Polyurethane foams are also non-transparent and characterized by high desorption of the chromophores from the pores of the material. Gelatin gels have low physical and mechanical properties. Ion-exchange sorbents are characterized by the complexity of synthesis and low kinetic characteristics of sorption.

Therefore, the search for new optically transparent materials with developed specific surface, chemical resistance and high physical and mechanical properties is an urgent task of polymer chemistry and materials science

2. Fundamentals of synthesis of mesoporous polymers based on aromatic isocyanates

Isocyanates are able to enter into chemical reactions leading to the formation of polymers with different structure. In most cases for the isocyanates, the reactions of nucleophilic addition of compounds containing mobile hydrogen atoms are typical. The reactions of isocyanates with diols and diamines are the most important from a practical point of view. In the presence of catalysts (tertiary amines, alkoxides and carboxylates of quaternary ammonium base, etc.) isocyanates go through dimerization and trimerization to form uretidinedions and isocyanurates [10]. The possibility of catalytic homopolymerization of isocyanates by anionic mechanism is also known. As a rule, polyisocyanates of amide nature are polyaddition products. However, in the literature [11] there is information about the formation of polyisocyanate links of acetal nature (O-polyisocyanates). The possibility of transformations in different directions is due to the ambident nature of the anion at the end of the growing chain (Figure 1). These works give the information about obtaining the polyisocyanate links of acetal structure by copolymerization of ethylene oxide and aromatic isocyanates using IR spectroscopy and chemical degradation of the polymer. Typical for these polymers, N = C bond appears in the IR spectra in the region of 1670-1680 cm^{-1} .

In [12,13] it was established that the open chain analogs of crown ethers, which are block copolymers of ethylene oxide and propylene oxide containing terminal and potassium alcoholate groups, are effective initiators of opening the isocyanate groups along the thermodynamically more stable carbonyl group. It was assumed that the capture of the metal cation by polyester fragment acting as a linear podand promotes the preferential localization of the negative charge on the oxygen atom of the growing chain in anionic polymerization. It was also shown that such polyaddition occurs only when 2,4-toluene diisocyanate is used involving isocyanate groups of more active para-position to the reaction process.

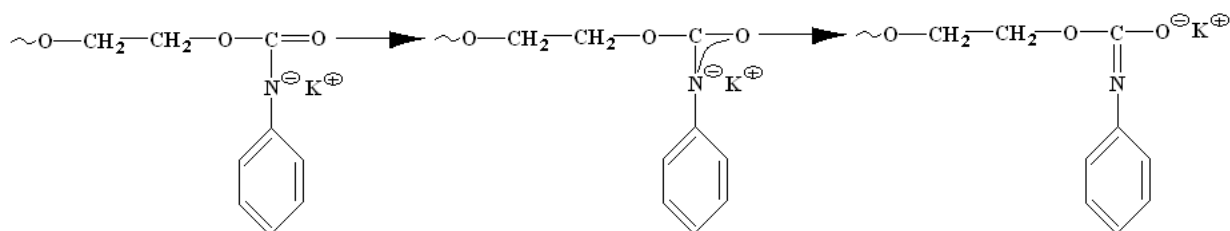
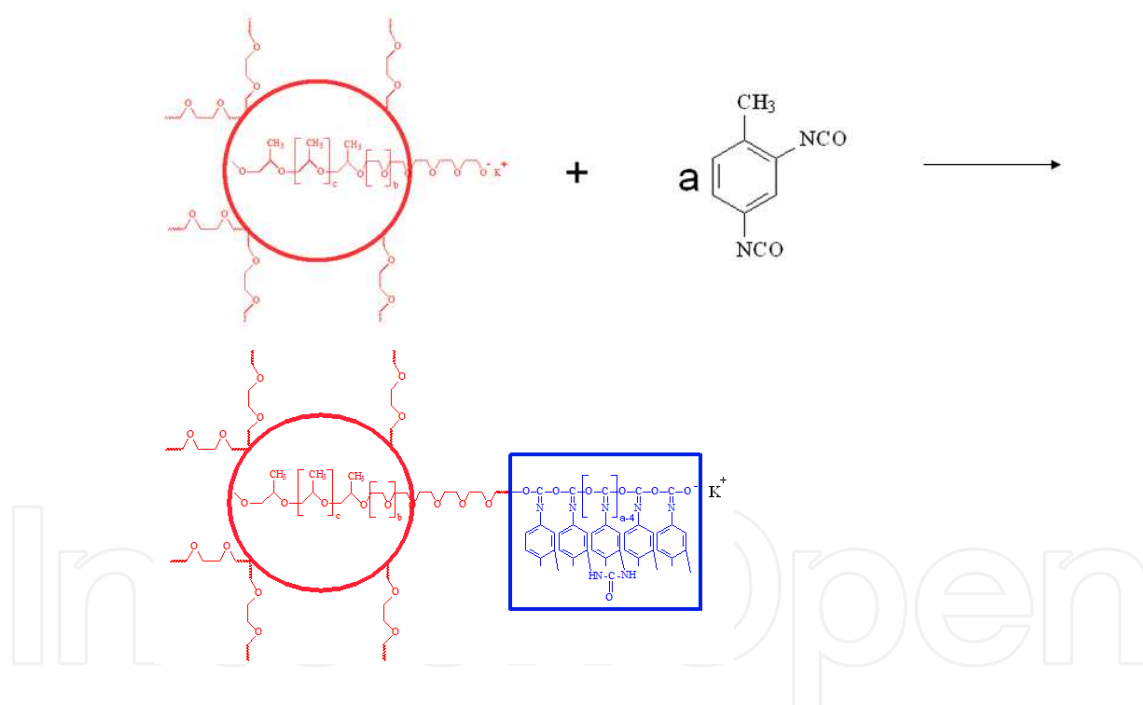


Figure 1. Ambident nature of the anionic center in the reaction of 2,4-toluene diisocyanate with alcoholates

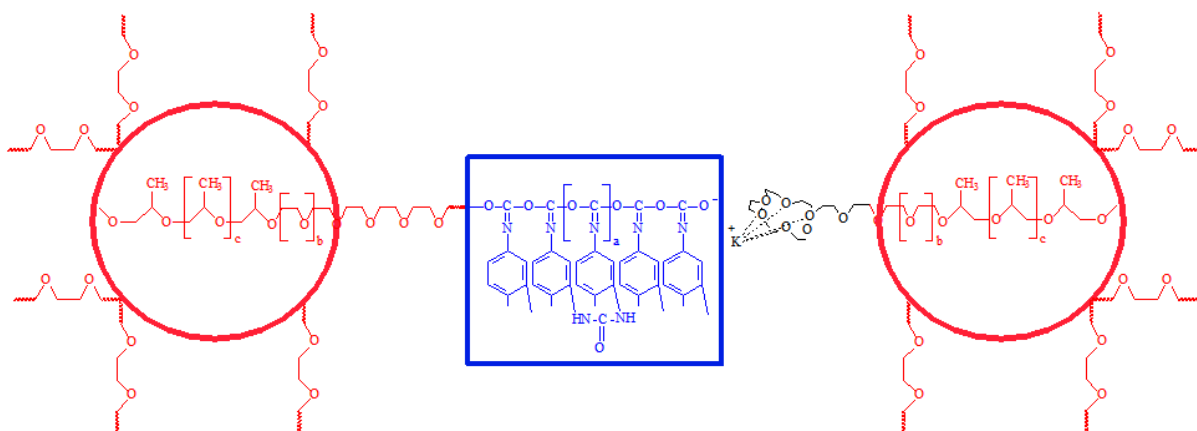
Open chain analogs of crown ethers, which are block copolymers of ethylene oxide and propylene oxide containing terminal potassium alcoholate groups turned out to be effective initiators of isocyanate groups opening by anionic mechanism. Previously, it was found that the opening of the isocyanate groups along the $N = C$ bond led to cyclization of polyaddition products with subsequent formation of polyisocyanurates. However, it turned out that if the macroinitiators were open-chain analogues of crown ethers there could be created favorable conditions for the opening of the isocyanate groups along the carbonyl component and the formation of the polyisocyanate structures of the acetal nature. Earlier in [14], it was shown that the polymers obtained in this way can reach the free volume up to 20% due to the formation of mesopores. Until now, there was uncertainty about the causes of the formation of transition pores in the volume of the polymer, the percentage of O-polyisocyanate blocks and how to manage the process in terms of creating the most favorable conditions for the formation of mesoporous polymers. According to the chemical structure of O-polyisocyanate links, their macroblocked structures are able to exhibit intense intermacromolecular interactions leading to their segregation.



Polymerization starts from a macromolecular coil representing the block copolymers of ethylene oxide and propylene oxide. Terminal reactive O-polyisocyanate units exhibit the ability to stabilize due to their interaction with forming structural fragments of crown ethers in the coil of macroinitiators.

In turn, the coil of macroinitiator is quite large, larger than 50 nm. The result is that the coil of macroinitiator contains a great number of macromolecules of open-chain analogs of crown ethers and is able to engender the growth of O-polyisocyanates' units as well as to stabilize the reactive terminal units.

In [15], it was shown that the involvement of the isocyanate groups in the *ortho*-position into the reaction with latent water with the following formation of urea groups contributed to stabilization of O-polyisocyanate blocks.



In this case the initiation and stabilization acquired rigorous multi-dimensional geometry in the space, the result of which was the cell structure with voids similar to honeycombs (Figure 2).

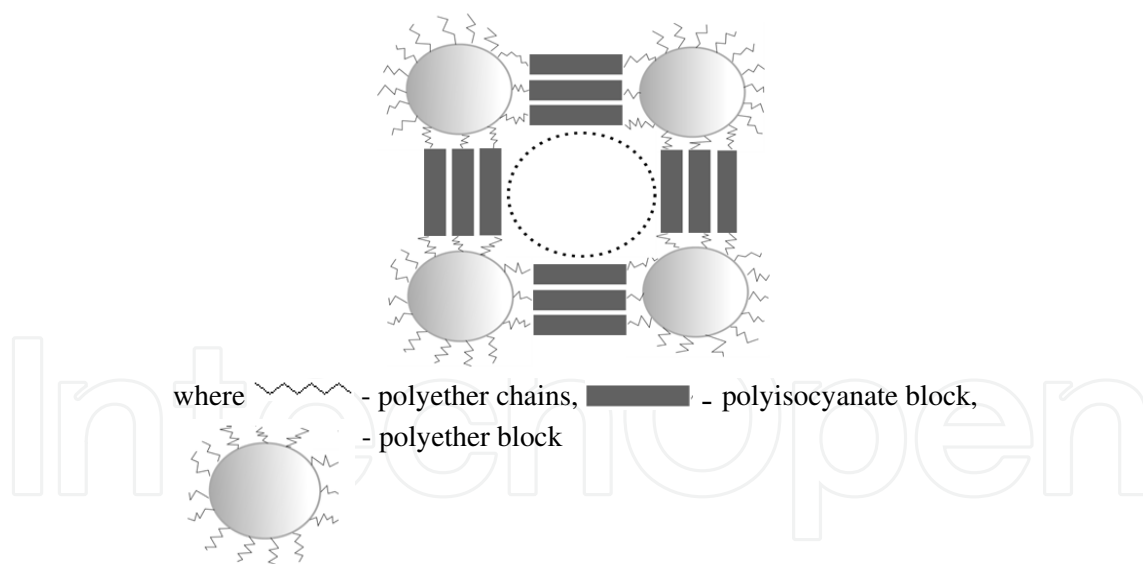


Figure 2. Scheme of the pores formation in the polymer based on anionic macroinitiator and 2,4-toluene diisocyanate

Evaluation of the sorption capacity of the polymers was carried out by water absorption. The adsorption isotherm of water vapor for the polymer sample was S-shaped, which is typical for polymers with transition pores (Figure 3). The specific surface area of sorbents was calculated by the equation proposed by Brunauer, Emmett and Teller and was 75 m²/g. According to [16], the specific surface of transitional pores (mesopores) is in the region of 20-200 m²/g.

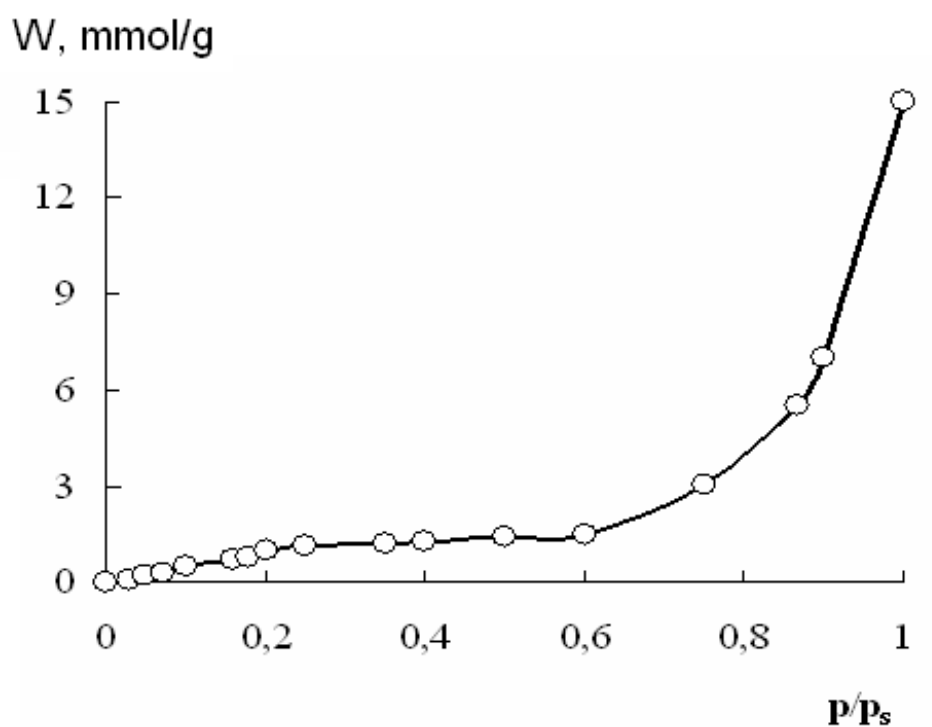


Figure 3. Water sorption curve for mesoporous polymer

Additional information about the processes of geometry of supramolecular structures in these polymers was obtained by using atomic force microscopy (Figure 4).

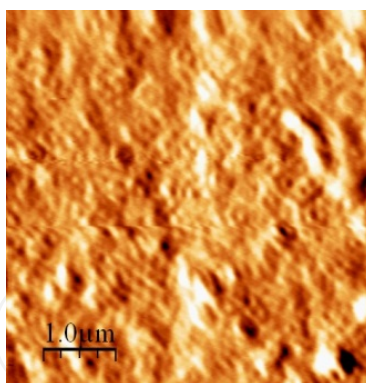


Figure 4. AFM image of a mesoporous polymer

3. Features of the organic chromophores immobilization in mesoporous polymers

Reactants, slightly soluble in water, are preferred, since the test-forms are more stable during storage and they are weakly leached from the test matrix during the contact with the test liquid.

When slightly water-soluble reactants are immobilized on the carriers, their solutions in organic solvents are used or the reagents are applied in the form of fine powder. To increase the binding strength of the agent with the carrier the chemical bonds are formed between them (chemical immobilization). For immobilization by covalent bonding (chemical immobilization) cellulose, polymers sorbents and silica gels are used as carriers. However, the "physical" fixing is usually much simpler, so it is quite widespread.

The presence of voids in the mesoporous polymer was the reason to immobilize organic polymer-supported reagents. The study of sorption processes of luminophores in polymers is of interest in connection with the possibility of obtaining laser media and sensors for photometric and luminescent determination of metal cations.

The study of the sorption properties of the polymeric material with respect to organic luminophores was carried out by electronic spectroscopy (Figure 5).

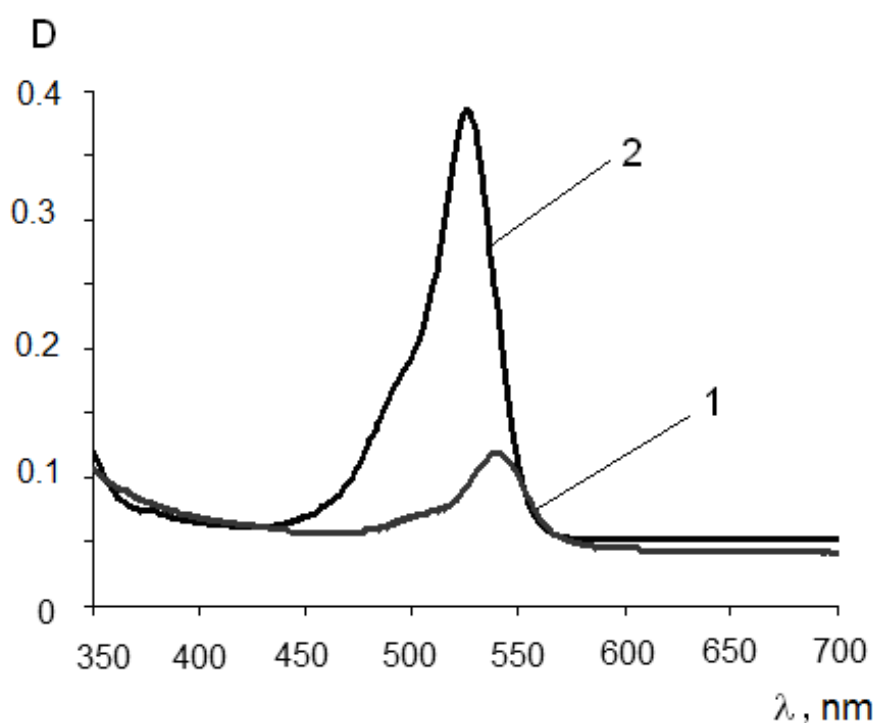


Figure 5. Electronic spectra of the solution of rhodamine 6G (1) in ethanol and rhodamine 6G, immobilized in the mesoporous polymer (thickness of the cuvette for the solution and the polymer sample was 0.1 cm)

As the luminophore rhodamine 6G (R6G) was selected and used to determine gold cations. A solution of R6G of the given concentration was obtained and the maximum value of the optical density was determined. According to the Bouguer-Lambert law the molar absorption coefficient for the solution of rhodamine 6G was calculated. Rhodamine 6G was sorbed on the polymer. The value of the optical density of the polymer sample doped with R6G at $\lambda_{\max} = 530$ nm was measured. The calculation of dye concentration in the polymer was performed. It was established that electron spectra of organic agents on polymer carriers did not have substantial changes in comparison with the spectrum of their solutions. It was established that adsorption

of organic phosphor 6G rhodamine is accompanied by its concentration of polymer matrix. The dye concentration in the polymer was 3 times more than in the initial solution. This fact points to the flow of intense adsorption of rhodamine 6G in the voids of the polymer.

4. Mesoporous polymers as laser active media

Dye lasers are used for spectroscopic studies to improve the sensitivity, spectral and temporal resolution by several orders of magnitude compared to traditional methods of spectroscopy. They can also be used where high energy of laser radiation is not needed. Typically, in dye lasers the solutions of dyes (solvents - water, alcohols, benzene derivatives, etc.), rarely dyes activated polymeric materials - polymethyl methacrylate, epoxy resin, polyurethane, etc. are used which are called polymeric laser-active media. However, these media have a number of drawbacks that make them difficult to use. For example, the polymer and dye undergo relatively rapid photodegradation, so the active medium often has to be changed.

Nowadays, thanks to the efforts of chemists and physicists, solid-state active media for tunable lasers are made with parameters as good as solutions' parameters. In recent years the interest in the emission of organic molecules in the thin films is growing due to the possibility of using them as the base for photoexciting microlasers and the materials for OLEDs. Polymers have great advantages over other materials. They show high optical uniformity, good compatibility with organic dyes and at the same time they are cheap and manufacturable. The latter facilitates the miniaturization and embeddability in optical systems.

Laser properties of mesoporous and nonporous polymers doped with rhodamine 6G dye were investigated for comparison. Because of specific samples forms it wasn't possible to measure laser efficiency directly. To estimate the laser efficiency, operating life-time amplified spontaneous emission (ASE) under transverse pump by the second harmonic of Q-switched Nd:YAG laser (pulsewidth was 12 ns, pulse repetition rate was 10 Hz) was measured. The pumping region had a form of a stripe with 27 μm width and length close to the sample length. Maximum intensity at the beam waist at the sample was 25 MW/cm^2 . The ASE was observed from two opposite samples cuts inside the cones with axis parallel to pump region in such setup configuration. The intensity of the ASE was measured from one side of the investigated sample with piroelectric energy sensor Ophir PE-9 (ASE was focused by spherical lens). Simultaneously from the other side of the sample ASE spectra were measured with wide-range spectrometer S100. At the pump intensity 25 MW/cm^2 the spectral half-width of the ASE didn't exceed 5 nm for all investigated samples (Figure 6).

Photostability of Rhodamine 6G in the mesoporous polymer at low pump energies (12.5 MW/cm^2) amounted to 115000 pulses, at high energies (25 MW/cm^2) - 60000 pulses. The energy of stimulated emission during irradiation reached maximum and then began to fall compared to the original value. The most widespread material for the solid-state polymer dye lasers is nonporous polymethylmethacrylate (PMMA). Therefore, the PMMA with R6G was chosen for comparison. Halving ASE energy of the PMMA doped with R6G was observed at around 200

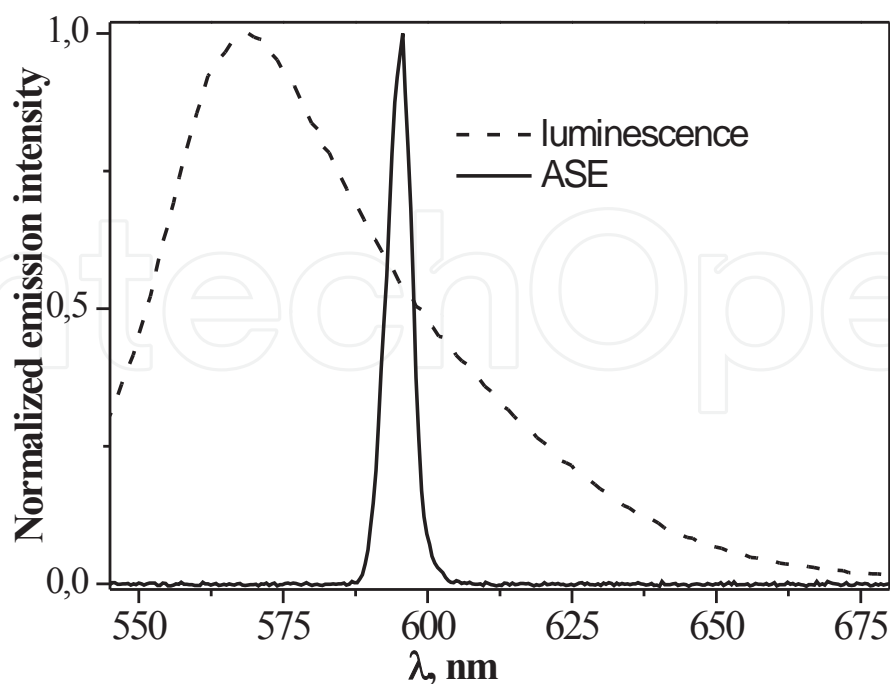


Figure 6. Luminescence (dash line) and ASE (solid line) spectra of the mesoporous polymer doped with rhodamine 6G

pulses, that is, about 175 times smaller than for the mesoporous polymer. PMMA demonstrates exponential ASE decay (Figure 7).

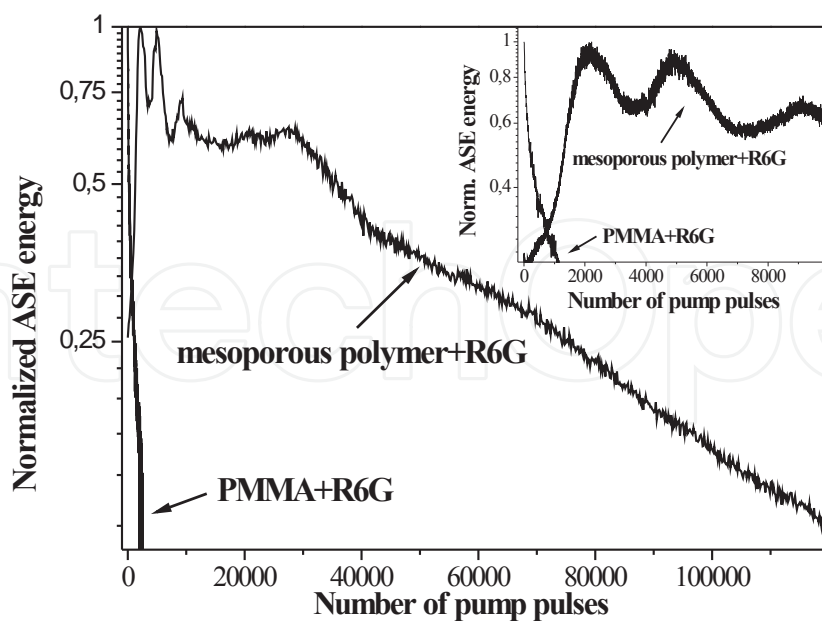


Figure 7. Dependences of the normalized ASE energy on the number of excitation pulses of mesoporous polymer and PMMA doped with R6G (pump intensity was 25 MW/cm²). The inset shows the details of the dependences at the beginning of the pump

Thus, the processes of generation of laser radiation and photochemical aging of organic luminophors in mesoporous and non-porous polymers were studied. It was shown that in the mesoporous polymers organic luminophors were able to generate laser radiation and high radiation resistance.

5. Mesoporous polymers as basis for optical chemical sensors

Organic chromophores react selectively with ions of many metals forming chelate complexes which are intensely colored. The reactions of complex forming organic chromophores and the ion being identified accompanied by color change of the reaction system are the foundation of chemical test methods on metal cations.

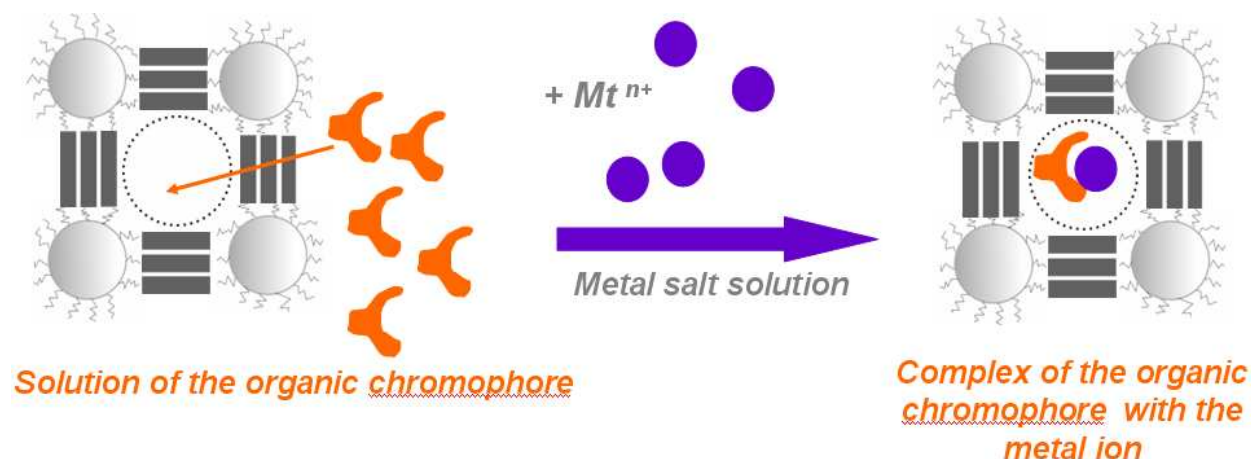


Figure 8. Scheme of the organic chromophore concentration and complex formation with metal ions in mesoporous polymers

In this work, as organic chromophores were used 1-(2-pyridylazo)-2-naphthol (PAN), arsenazo III and phenazo as reactants, soluble salts of copper CuSO_4 and cobalt CoCl_2 , manganese MnCl_2 , lanthanum LaCl_3 , calcium CaCl_2 , magnesium MgCl_2 as analytes.

Organic chromophores arsenazo III, phenazo and 1-(2-pyridylazo)-2-naphthol (PAN) have the chemical structure shown in Figure 9.

Immobilization of the organic reagent PAN on mesoporous carriers was carried out by its adsorption from solution in ethanol. It was found that the electron spectrum of PAN on the polymeric carrier was not changed significantly compared with the spectrum of its solution (Figure 10).

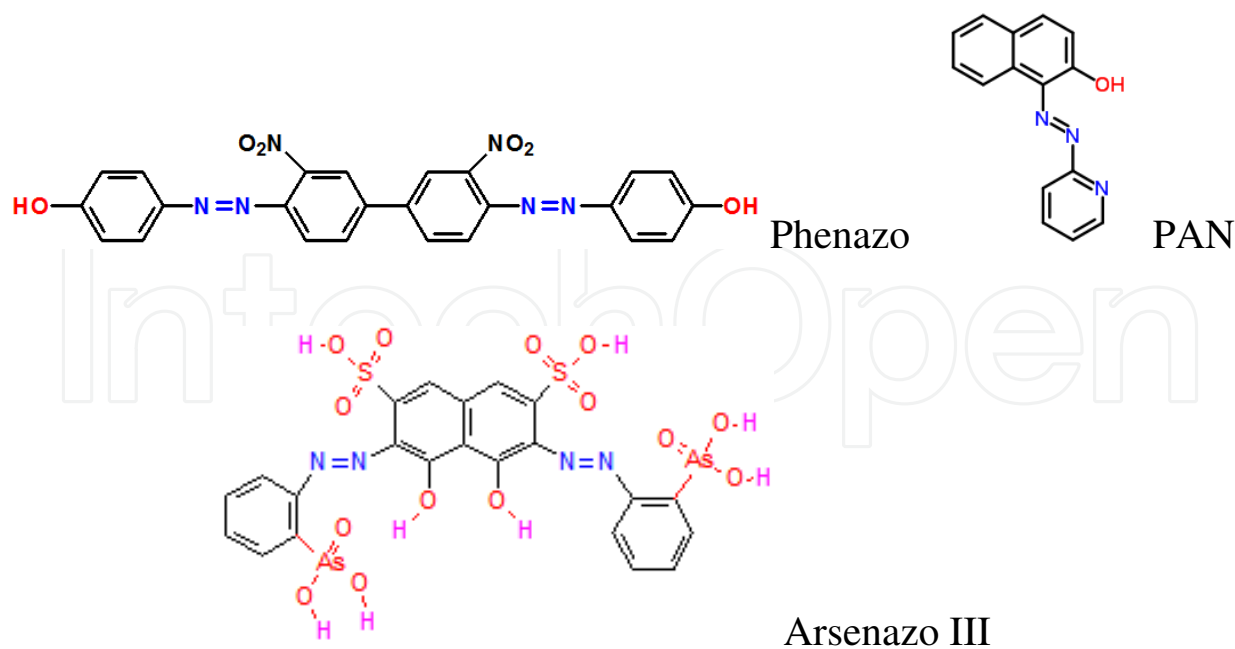


Figure 9. The chemical structure of organic chromophores

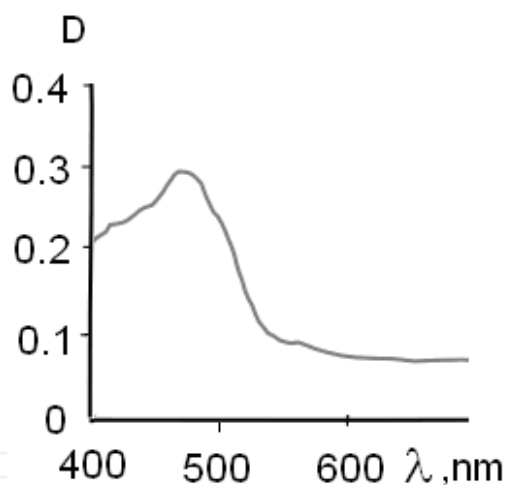


Figure 10. The electronic spectrum of PAN in the mesoporous polymer

To determine the sensitivity limits of complexing reactions of organic reagent with metal cations a series of solutions with salt concentrations 10^{-1} g/l, 10^{-2} , 10^{-3} g/l, 10^{-4} g/l and 10^{-5} g/l was prepared. Polymeric carriers modified with organic reagent were kept in solutions of respective salt for one hour.

Complexes of copper and PAN, PAN and manganese stained polymer in red, complex of cobalt and PAN stained in purple. The value of λ_{\max} of PAN complexes with metals when it transferred from solution to mesoporous polymers was not changed. The analysis of the absorption spectra shown in Figures 11 and 13, revealed that 1-(2-pyridylazo)-2-naphthol in mesoporous

polymers was able to interact with the metal cations. The height of the characteristic band of the complex PAN - metal depends on the concentration of metal in solution, which further will allow to carry out not only qualitative but also quantitative analysis of metal content.

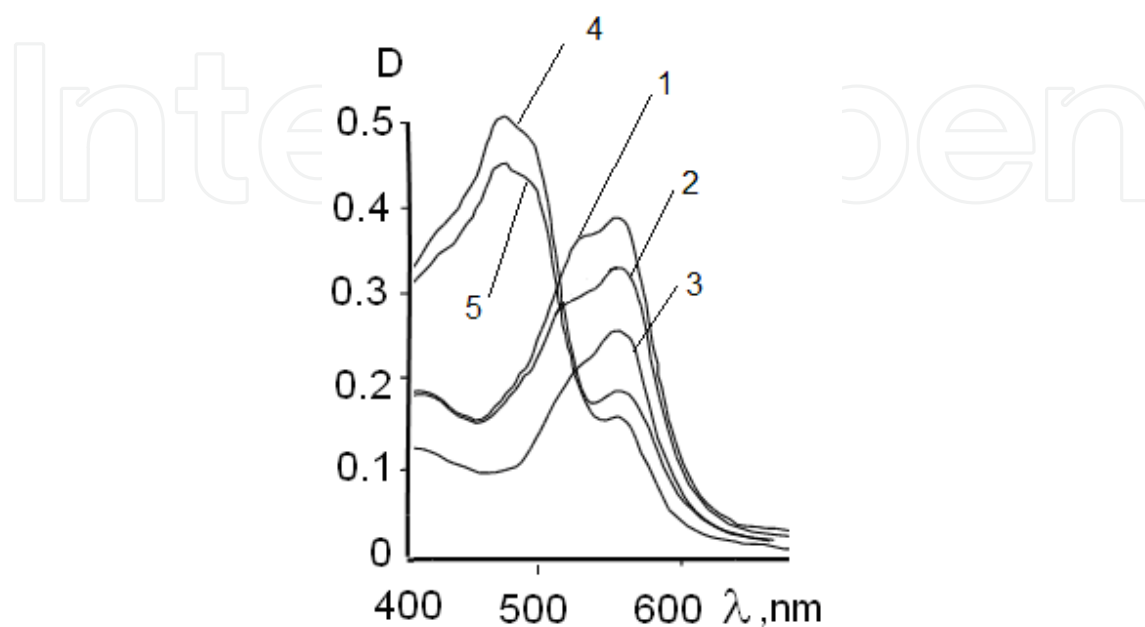


Figure 11. Electronic spectra of the Cu - PAN complex, immobilized in a mesoporous polymer by adsorption from solution,

$[\text{CuSO}_4] = 10^{-1}$ g/l (1), 10^{-2} g/l (2), 10^{-3} g/l (3), 10^{-4} g/l (4), 10^{-5} g/l (5)

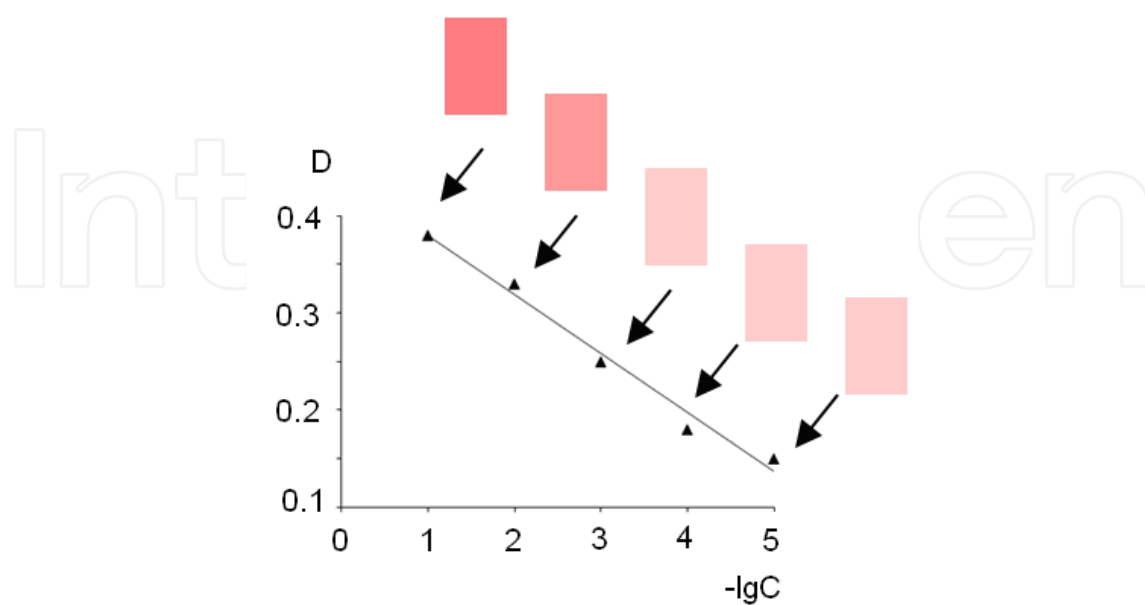


Figure 12. The calibration curve for the Cu - PAN complex in the mesoporous polymer

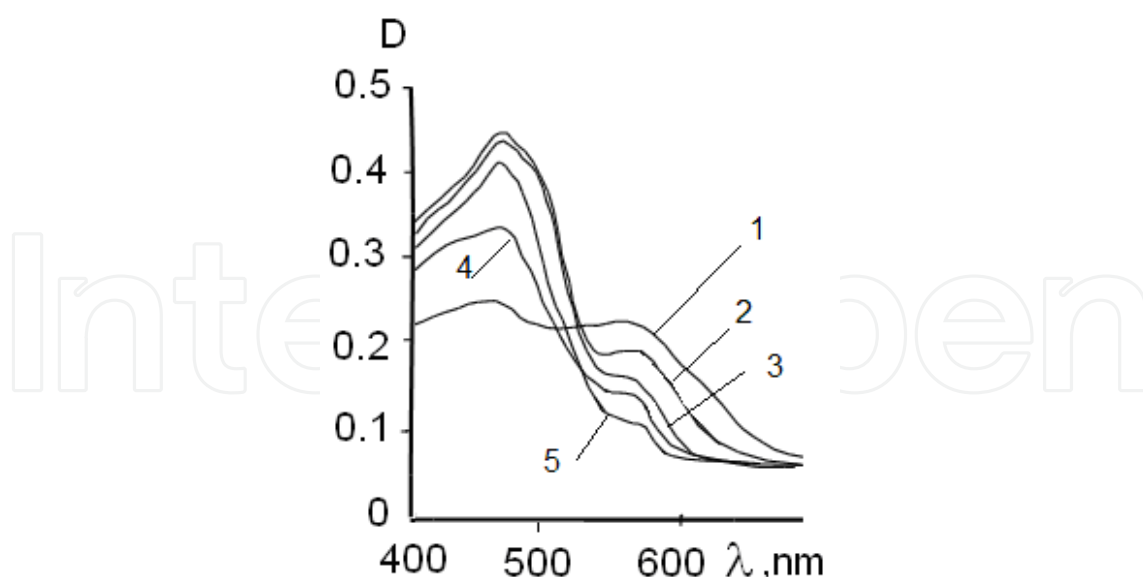


Figure 13. Electronic spectra of the Co - PAN complex, immobilized in a mesoporous polymer by adsorption from solution,

$[\text{CoCl}_2] = 10^{-1}$ g/l (1), 10^{-2} g/l (2), 10^{-3} g/l (3), 10^{-4} g/l (4), 10^{-5} g/l (5)

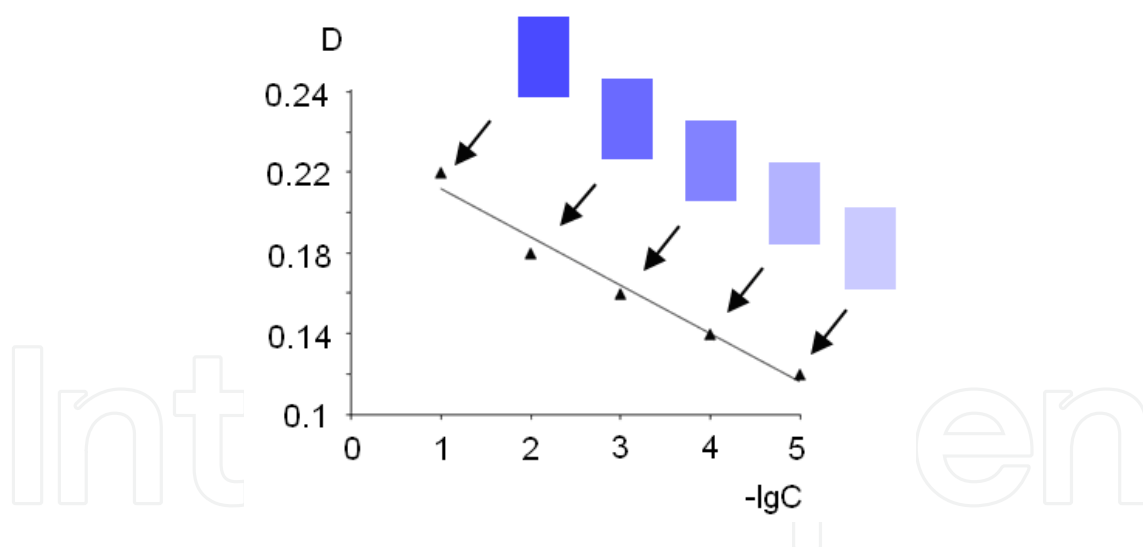


Figure 14. The calibration curve for the Co - PAN complex in the mesoporous polymer

The analysis of the absorption spectra and calibration curves shown in Figures 10 - 14 for 1-(2-pyridylazo)-2-naphthol in mesoporous polymers revealed that the sensitivity of the complexation reaction of PAN and manganese cations on solid carriers was 10^{-5} g/l.

Phenazo chromophore forms with magnesium in alkaline medium an adsorption compound of blue-purple color, the reagent solution is painted in crimson. The absorption maxima of reagent and its complex with magnesium are observed at 490 and 560 nm, respectively. For

the reagent and compound with magnesium a molar absorption coefficient is 13900 and 35400, respectively [20]. The optimum concentration of NaOH is 1-2N. Colouring of magnesium compound is stable for 1 hour.

Phenazo's spectra and its complexes with magnesium adsorbed in the pores of the polymer are shown in Figure 15. The limit of sensitivity of complexation reaction of chromophore with magnesium in this case was 10^{-5} g/l.

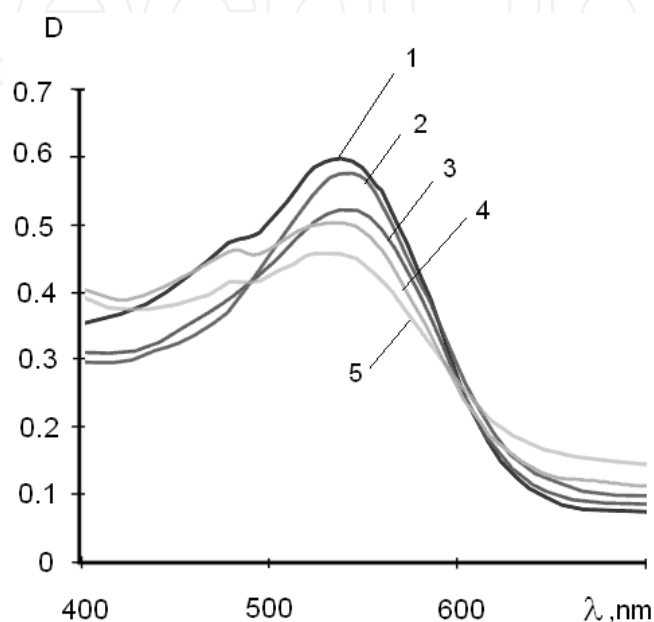


Figure 15. Electronic spectra of the Mg - Phenazo complex, immobilized in a mesoporous polymer by adsorption from solution,

$[MgCl_2] = 10^{-1}$ g/l (1), 10^{-2} g/l (2), 10^{-3} g/l (3), 10^{-4} g/l (4), 10^{-5} g/l (5)

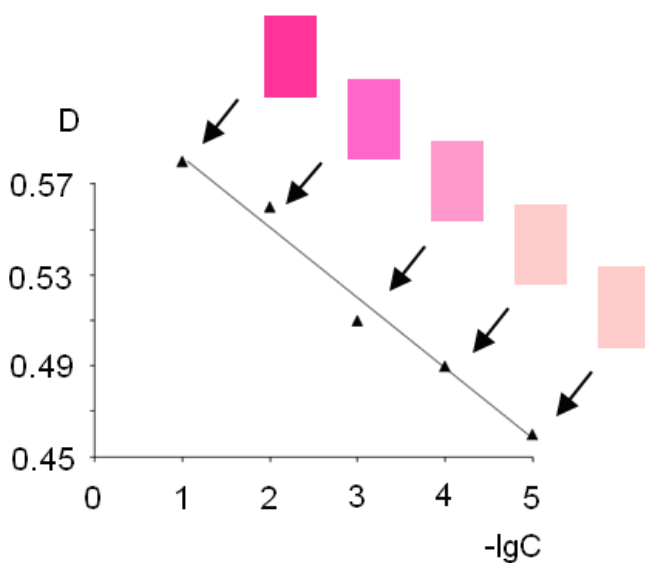


Figure 16. The calibration curve for the Mg - Phenazo complex in the mesoporous polymer

The main feature of the reagent arsenazo III is its ability to form very strong chelates with elements. The good contrast of complexes and large values of molar absorption coefficient ($50 \cdot 10^3 - 130 \cdot 10^3$) along with the ability to reach high dilutions without dissociation of complexes provides high sensitivity of reactions - up to $0.01 \mu\text{g/ml}$.

A maximum of the electronic spectrum of arsenazo III corresponds to a wavelength of 540 nm. From the literature [20], it is known that the absorption spectra of the complex of lanthanum with arsenazo III have the maximum at wavelength of 665 nm and a molar extinction coefficient of the complex $4.5 \cdot 10^4$, the maximum of the absorption spectrum of the complex of calcium and arsenazo III occurs at the wavelength of 655 nm, the molar extinction coefficient of complex is 10^4 .

Figure 17 shows the electronic spectrum of mesoporous polymer-modified arsenazo III. The spectrum does not change much compared to the spectrum of an aqueous solution of arsenazo III. Modified films were studied as an analytical sensor for detecting lanthanum and calcium. Figures 18 and 20 show the electronic spectra corresponding to the complexes of arsenazo III with calcium and lanthanum. It was found that complexes of arsenazo III with lanthanum and calcium, immobilized on a polymer, have clearly expressed characteristic bands on the electronic spectra. In case of the complex arsenazo III - calcium the bands at 600 and 655 nm are observed, for the complex arsenazo III - lanthanum the bands appear at 605 and 665 nm.

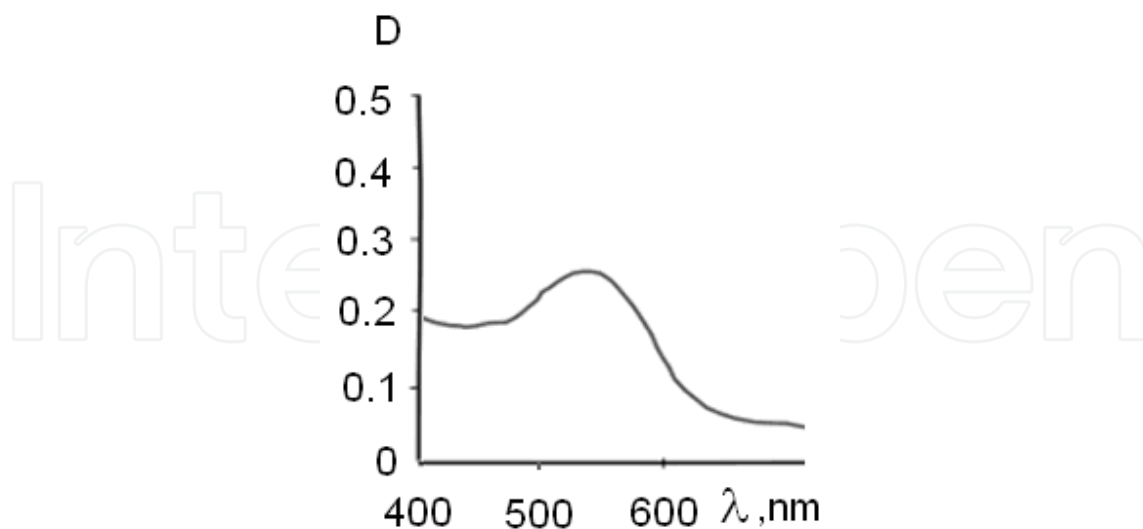


Figure 17. The electronic spectrum of arsenazo III in the mesoporous polymer

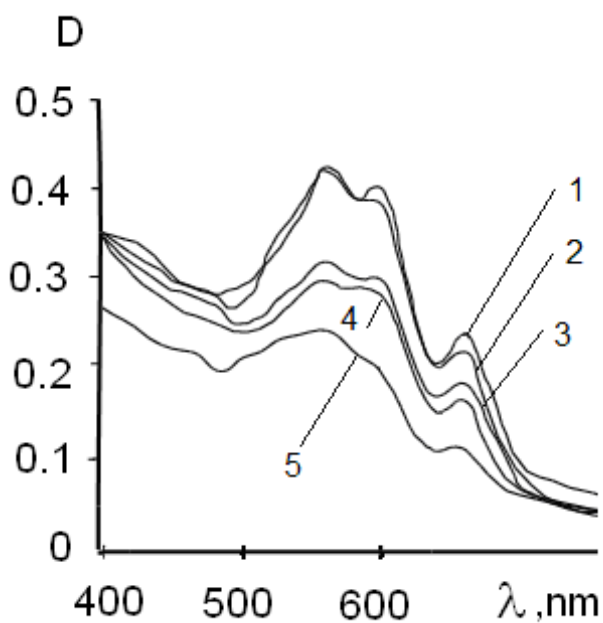


Figure 18. Electronic spectra of the Ca - Arsenazo III complex, immobilized in a mesoporous polymer by adsorption from solution,

[CaCl₂]= 10⁻¹ g/l (1), 10⁻² g/l (2), 10⁻³ g/l (3), 10⁻⁴ g/l (4), 10⁻⁵ g/l (5)

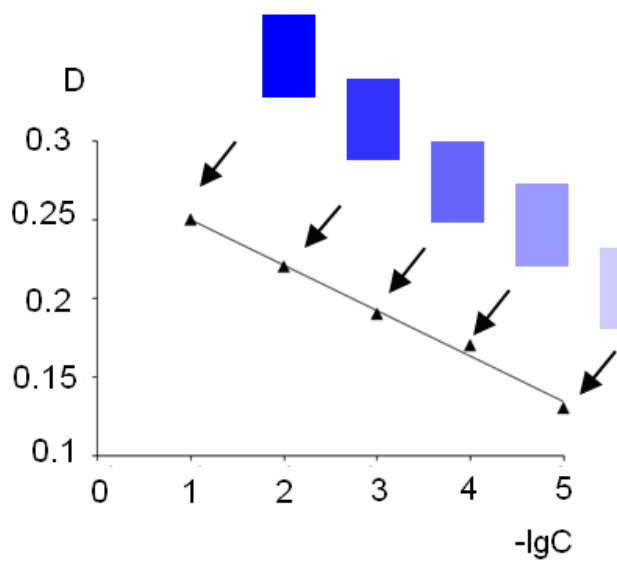


Figure 19. The calibration curve for the Ca – Arsenazo III complex in the mesoporous polymer

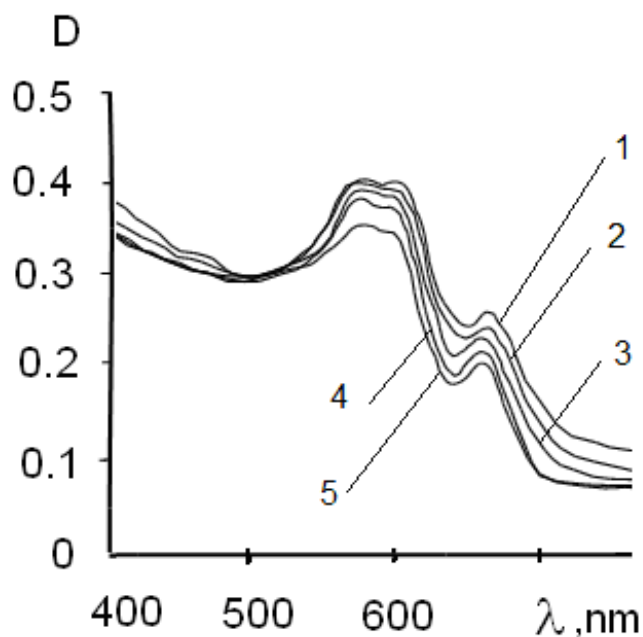


Figure 20. Electronic spectra of the La - Arsenazo III complex, immobilized in a mesoporous polymer by adsorption from solution,

$[\text{LaCl}_3 \cdot 6\text{H}_2\text{O}] = 10^{-1} \text{ g/l}$ (1), 10^{-2} g/l (2), 10^{-3} g/l (3), 10^{-4} g/l (4), 10^{-5} g/l (5)

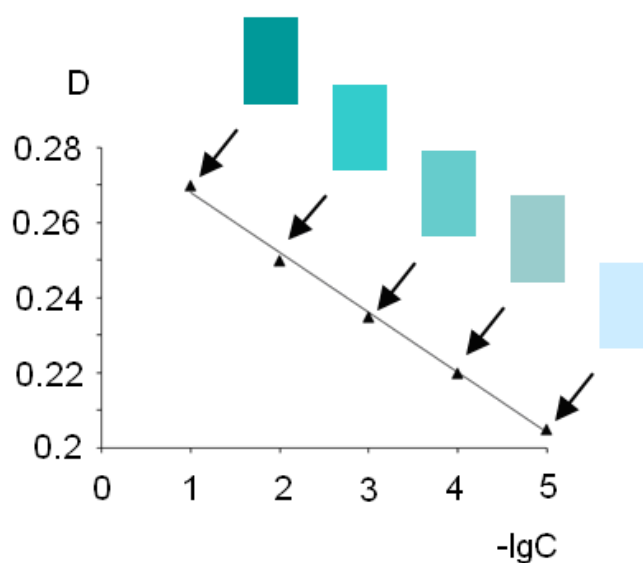


Figure 21. The calibration curve for the La - Arsenazo III complex in the mesoporous polymer

For the polymer matrix modified with arsenazo III, the limit of sensitivity to calcium and lanthanum ions was determined. The maximum concentration at which the metal ions were detected was 10^{-5} g/l.

6. Conclusion

Optically transparent mesoporous block copolymers with regulated free volume were obtained by polyaddition of 2,4-toluene diisocyanate to anionic macroinitiators. It is established that the void formation is conditioned by the geometry of block copolymer self-assembly.

It is established that the chemical nature of a solvent influences the mechanism of polyaddition of 2,4-toluene diisocyanate to the anionic macroinitiator which is a potassium substituted block copolymer of propylene oxide with ethylene oxide.

It is shown that ethyl acetate is the most advantageous solvent for the predominant formation of O-polyisocyanate blocks during the polyaddition of 2,4-toluene diisocyanate to the anionic macroinitiator.

Polymer laser active media based on mesoporous polymers doped by organic luminophores were obtained. The possibility is shown to obtain the induced emission of Rhodamine 6G in mesoporous polymers. It is shown that photochemical stability of organic chemical agent and luminophor rhodamine 6G in polymers made up more than 70,000 pulses.

It was shown that the polymer mesoporous structure provides the possibility to immobilize organic chromatophores in mesoporous polymers. It was established that adsorption processes of organic luminophore of rhodamine 6G were accompanied by the processes of its concentration in a polymer matrix.

The polymer laser-active media based on mesoporous polymers doped by organic chromatophores were obtained. The possibility to obtain the induced emission of radiation of rhodamine 6G in mesoporous polymers was shown. It was also shown that photochemical stability of an organic reagent and luminophore of rhodamine 6G in polymers made up 70.000 pulses.

The qualitative reactions of organic chromatophores arsenazo III, PAN, and phenazo with metal cations on a mesoporous polymer carrier were carried out. It was shown that reaction sensitivity of complex formation of metals and chromatophores on mesoporous polymer substrate made up 10^{-5} g/l.

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