

PHYSICAL CHEMISTRY OF NANOCCLUSERS AND NANOMATERIALS

The Formation of Porous Nickel-Containing Polyacrylate Nanocomposites

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Abstract—The formation of porous nickel–polyacrylate nanocomposites (the sorption of nickel ions by a polyacrylate matrix followed by their reduction with thiourea dioxide) was studied. The kinetics of sorption of nickel ions was determined, and the diffusion coefficient was found using the method of a moving boundary. Transmission electron microscopy was used to establish the size and distribution of nickel nanoparticles in a porous matrix depending on synthesis conditions. The localization of nanoparticles only inside polymer pores was shown to be determined by a decrease in the barrier to nucleation because of the heterogeneous nucleation mechanism. Nickel nanoparticles stabilized by polyacrylates can be used to decrease the intensity of high-power laser radiation.

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INTRODUCTION

Metal nanoparticles offer promise for use in nonlinear optics [1], catalysis [2], and other domains of science and technology. Their use in practice as a rule encounters the problem of the immobilization of unstable and nonequilibrium particles in matrices with a high specific surface area, which ensure accessibility to reagents and the removal of reaction products, that is, in structured systems containing open connected pores with various diameters. The synthesis of metal nanoparticles in nanoporous media is performed in situ (in the presence of carrier matrices) [3]. Small-sized pores, however, decelerate the diffusion of reagents. For this reason, carriers with large-sized pores are often required for practical applications.

The preparation of block nanocomposites filled with metal nanoparticles is, in particular, performed by the reduction from ions introduced into pores of polymer or inorganic matrices [4–6]. Macropores play the role of a peculiar reactor. The nature of their surface and structure influences the localization and size of product particles. However, in spite of practical results obtained, the mechanism of formation and stabilization of metal nanoparticles in matrices with pores having sizes of several dozens to hundreds nanometers has not been studied in detail.

This work is concerned with processes resulting in the formation and stabilization of nickel nanoparticles inside block polymer matrix macropores. We used polyacrylates containing carboxyl groups as matrices; these groups are capable of coordinating metal ions. Thiourea dioxide was used as a reducing agent. Thiourea dioxide can be used for the preparation of nickel-containing solutions stable at room temperature for a

long time sufficient for the introduction of solutions into polymer pores.

EXPERIMENTAL

The block porous polymer matrix was prepared by the copolymerization of methyl methacrylate (MMA) with potassium methacrylate (PMA) in the presence of a pore forming agent (polyethylene glycol PEG-200). Benzoyl peroxide was used as an initiator, and the reaction was performed at 70°C [4]. The polymer structure formed after the removal of the pore forming agent in a Soxhlet apparatus. The molar ratio between the components of the mixture to be polymerized was [MMA] : [PEG] : [PMA] = 1 : 0.4 : 0.2. Block polymer samples were 3 mm thick. The concentration of carboxyl groups in them was determined by potentiometric titration at 20°C. The degree of polymer swelling was studied volumetrically. The small-angle X-ray diffraction patterns of the dry polymer matrix were obtained on a SIEMENS diffractometer. The morphology of the surface was studied using a Philips SEM 515 scanning electron microscope. The kinetics of sorption of nickel ions was determined at a 0.24 mol/l concentration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ over the temperature range 20–70°C. Three parallel experiments were performed. The diffusion coefficient of nickel ions in the polymer matrix was calculated using the method of a moving boundary by the equation

$$c(x, t) = c_0 \frac{2}{\sqrt{\pi}} \text{erf} Z, \quad Z = x/2(Dt)^{1/2}, \quad (1)$$

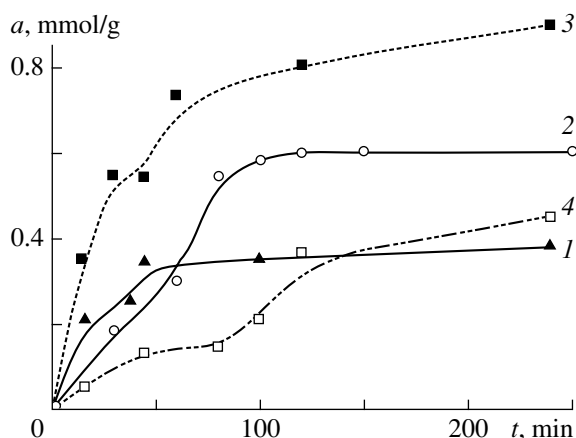


Fig. 1. Kinetic curves of the sorption of nickel ions by a polyacrylate matrix at (1) 20, (2) 30, (3) 50, and (4) 70°C; α is the sorption capacity.

where $c(x, t)$ and c_0 are the concentrations of nickel ions in the matrix and solution, respectively; $\text{erf}Z$ is the error integral; t is the time of sorption; x is the diffusion path; and D is the diffusion coefficient [7, 8]. To determine the diffusion path, the surface of block samples except one face was isolated from the environment, and the samples were placed into an aqueous solution of nickel chloride. The diffusion path was measured with the use of an optical microscope. The content of nickel in the polymer was determined photometrically on a KFK-3 photometer following the standard procedure [9] after the thermal decomposition of the sample and the solution of the dry residue.

The reduction of nickel ions in the porous polymer volume was performed at 20 and 80°C after the sorption of the reagents by the polymer matrix from an aqueous solution containing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 mol/l) and thiourea dioxide $(\text{NH}_2)_2\text{CSO}_2$ (TUDO) (0.24 mol/l) at 0°C for 4 h. The IR spectra of polymeric samples were recorded on a Nicolet 5700 spectrometer. The size and distribution of nickel nanoparticles in the polymer were studied on a JEM-100CXII (JEOL), 80 keV, transmission electron microscope.

The kinetics of reduction of nickel ions with TUDO in the presence of methyl methacrylate and potassium polymethacrylate (PPMA) was studied in an aqueous solution at 20°C by cyclic voltammetry. The component concentrations in solution were $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.006 mol/l; PPMA, 0.012 mol/l; and TUDO, 0.1 mol/l. TUDO was added 10 min after the introduction of nickel chloride and PPMA. To stop the reaction and release nickel ions, HClO_4 (0.1 M, 1 ml) was added to the solution. We used a PU-1 polarograph with a two-electrode cell. The reference electrode was a silver-chloride electrode, and a silver wire with a suspended mercury drop at its end was the indicator electrode. The mercury drop with a constant diameter was prepared electrolytically from a saturated solution of mercury nitrate. The voltammetric dependences were recorded

in the differential mode of potential changes at a rate of 30 mV/s. The range of potentials studied was from -1.2 to $+0.1$ V.

The absorption spectra of solutions were recorded on an SM 2203 (Belarus) spectrophotometer. The transmission of aqueous solutions of nickel chloride, thiourea, PPMA, and dispersion containing nickel particles was studied using focused laser radiation (Nd : YAG laser, the second harmonic, $\lambda = 532$ nm, $t_{\text{pulse}} = 12$ ns, $W = 150$ MW/cm²). The procedure was described in detail in [1].

RESULTS AND DISCUSSION

The formation of the porous structure of the polymer matrix occurs as a result of microphase layering during polymerization; it was described in detail in [4, 5]. The scanning electron microscopic image of the surface of the swollen polymer matrix shows the presence of pores 100–400 nm in diameter. Small-angle X-ray scattering studies of the dried polymer matrix showed [5] that the internal structure of the copolymer was a combination of distributed inhomogeneities (with respect to electron density) with sizes of from 2 to 50 nm. The size distribution shows the predominance of very small and very large inhomogeneities with a moderate fraction of intermediate inhomogeneities. Small-sized inhomogeneities are associates of copolymer ionic (carboxyl) groups. Spherical macropores that appear after the extraction of polyethylene glycol are large-sized inhomogeneities. The surface of pores contains carboxyl groups, which make the polymer capable of binding metal ions. Carboxyl groups present in the gel phase are responsible for polymer swelling and permeability in the moist form. Drying causes sample shrinkage and a decrease in the size of pores. Such polyelectrolyte gels containing spherical pores (their properties were studied in [10]) are known as “Swiss cheese.” The concentration of accessible carboxyl groups in the polymer determined by potentiometric titration was 0.57 mmol/g. The diffusion coefficient of Ni^{2+} ions in the volume of the polyacrylate matrix calculated by (1) was 3×10^{-7} cm²/s. Such a low diffusion coefficient value (more than 20 times lower than the diffusion coefficient of Ni^{2+} in aqueous solution) is evidence of the absence of through channels in the gel phase. Pores can therefore conventionally be considered closed.

The step character of the kinetic dependences of the sorption of nickel ions by the polymer matrix (Fig. 1) leads us to suggest that, at the initial stage of sorption, the binding of nickel ions by copolymer carboxyl groups occurs; next, their nonexchange absorption by macropores takes place. The amount of nickel ions that can be coordinated by polymer accessible functional groups (their concentration was found to be 0.57 mmol/g) was ~ 0.25 mmol/g polymer (measurements at 20°C). The divalent nickel ion is likely coordinated by two carboxyl groups, which replace either chloride ions or

water molecules present in the inner coordination sphere of the $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ complex.

Studies of the sorption of nickel ions from solutions held at various temperatures showed that an increase in temperature to 50°C increased the amount of sorbed nickel. This can be explained by an increase in the number of accessible carboxyl groups. The inflection of kinetic curves then shifts toward higher nickel ion concentrations. The time of the attainment of the equilibrium concentration in the polymer/solution system also increases. As the temperature of sorption grows to 70°C , the amount of sorbed nickel ions decreases sharply, and the inflection shifts to a lower nickel concentration. The rate of sorption also decreases substantially.

A comparison of these data with the degree of polymer swelling after the attainment of the equilibrium concentration of nickel ions (table) leads us to suggest that Ni^{2+} ions can effectively cross-link the polymer gel. As the density of the gel network increases, its swelling decreases, and the diffusion of ions occurs much more slowly. At temperatures above 50°C , gel collapse occurs, which sharply decreases its sorption capacity. A similar effect was observed for thermosensitive gels based on polyacrylates. It is explained by strengthening of interactions between hydrophobic polymer chains [11]. The amount of nickel ions bound by polymer carboxyl groups was determined from the position of curve inflections, the results are listed in the table. We found that it was insignificantly larger than the amount of ions absorbed by the nonexchange mechanism.

The IR spectrum of the polymer matrix contains a band of asymmetric free CO_2^- group vibrations at 1574 cm^{-1} (Fig. 2, spectrum 1), which is evidence of the presence of ionic associates. This is substantiated by the small-angle X-ray scattering data. After the sorption of nickel ions, the intensity of the peak at 1574 cm^{-1} decreases. At the same time, a peak of the coordinated CO_2^- group appears at 1612 cm^{-1} (Fig. 2, spectrum 2). The band of symmetrical free carboxyl group vibrations is observed at 1482 cm^{-1} ; it shifts to 1484 cm^{-1} after the coordination of nickel ions. The large difference between the frequencies of asymmetric and symmetrical carboxyl group vibrations $\Delta = [\nu_a(\text{CO}_2^-) - \nu_s(\text{CO}_2^-)] = 128\text{ cm}^{-1}$ is evidence of the bridge coordination of nickel ions [13, 14].

The second stage of the synthesis of metal–polymer nanocomposites is the reduction of nickel ions sorbed by the polymer. The reduction of nickel ions by the sulfur-containing reagent, thiourea dioxide, in solutions was studied in detail in [15–17]. The activation energy of reduction $E_a = 149\text{ kJ/mol}$; that is, the rate of reduction strongly depends on temperature. Thanks to this, we can prepare TUDO–Ni(II) solutions stable at reduced temperatures and perform simultaneous sorption of nickel chloride and the reducing agent by the

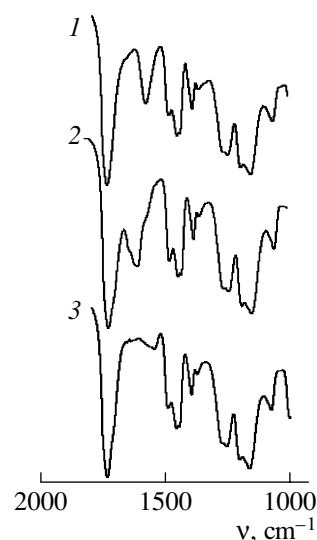


Fig. 2. Fragments of the IR spectra of (1) the initial polymer matrix, (2) matrix after the sorption of nickel ions from a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and (3) matrix after the reduction of nickel ions with TUDO.

polymer matrix. The rate of reduction sharply grows as the temperature increases to 40°C , and 60% of nickel chloride precipitates in the form of a powder of $0.3\text{--}0.5\text{ }\mu\text{m}$ particles containing 99.9% nickel [16]. This makes TUDO a suitable reducing agent for the synthesis of block composites with a uniform distribution of nickel particles over the volume.

When a block polymer sample is introduced into a stable solution containing nickel chloride and TUDO in the concentrations specified above, the reduction of nickel ions in the polymer volume begins as the components diffuse into the matrix, and we observe sample darkening. At the same time, the solution remains stable. At sorption temperature of 0°C , no reduction of nickel ions was observed in the volume of the sample. For this reason, sorption was performed at this temperature. After sorption completion, samples were placed into dodecane and heated to 20 and 80°C .

According to the transmission electron microscopic data, particles formed in the matrix after the reduction

Sorption characteristics of polyacrylate matrix

$T, ^\circ\text{C}$	a_{max}	N	τ	θ
20	0.35	65	100	365
30	0.60	55	110	355
50	0.90	65	280	280
70	0.50	35	320	150

Note: a_{max} is the maximum sorption capacity with respect to Ni^{2+} , mmol/g; N is the number of Ni^{2+} ions absorbed by the exchange mechanism, %; τ is the time of equilibrium establishment, min; and θ is the degree of swelling, %

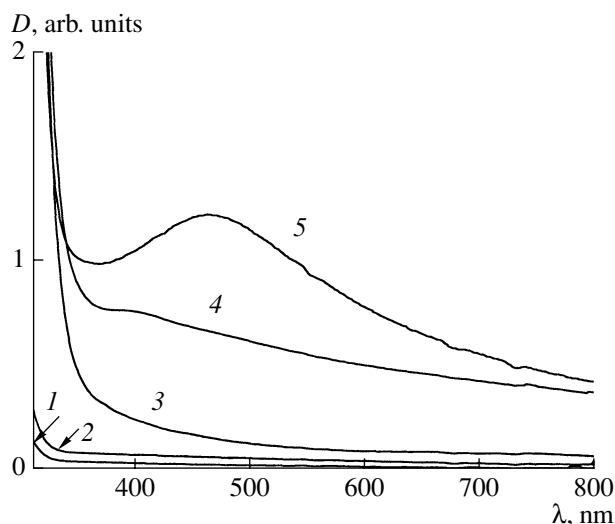


Fig. 3. Spectra of solutions containing (1) nickel chloride (0.006 M), (2) potassium polymethacrylate, (3) a mixture of Ni^{2+} and PPMA in similar concentrations, (4) the same solution 5 min after the addition of TUDO, and (5) the same solution 125 min after the addition of TUDO.

of nickel ions formed agglomerates uniformly distributed over the polymer. The size of agglomerates formed when samples were heated to 20 and 80°C was 40–60 nm, which corresponded to the size of pores in dry samples. This leads us to suggest that reduction is localized inside or on the surface of polymer pores, although nickel ions are also present in the gel phase. The localization of reduction on the surface of pores can be caused by a decrease in the work of critical cluster formation on the surface, $\Delta G_{\text{crt}} = GK(\alpha)$, where $K(\alpha) = (1/4)(2 + \cos\theta)(1 - \cos\theta)^2$, θ is the contact angle between the cluster and pore surface, and α is the density of free surface energy of cluster formation [3]. The number of particles in an agglomerate formed at 80°C is larger; their mean size determined by measurements of 30 objects is 17 ± 5.7 nm. The size of particles formed at 20°C is 13 ± 3.4 nm.

The IR spectrum of the nickel/polyacrylate nanocomposite (Fig. 2, spectrum 3) obtained at 80°C contains a band of carboxyl group asymmetric stretching vibrations shifted to 1540 cm^{-1} . Its intensity decreases substantially, likely because of partial decarboxylation also observed in [5]. The distance between the symmetrical and asymmetric vibration frequencies is 57 cm^{-1} , which is characteristic of chelate bidentate coordination. Coordination can involve unreduced nickel ions. There can also be the adsorption of the polymer (through carboxyl groups) on the surface of nickel particles, which prevents them from aggregation and causes their stabilization. A limited number of nickel ions inside a pore results in a limited particle size r_{max} starting with which the further growth of the particle becomes unfavorable energetically [3].

The reduction of nickel ions in the polymer is difficult to study because the reagents cannot be rapidly got from a block sample for analytic purposes. Studies were therefore performed in an aqueous solution containing not only nickel ions but also PMA and PPMA synthesized following the standard procedure [18]. To determine the order of the reaction with respect to nickel ions, excess reducing agent was introduced.

When PPMA was introduced into the solution containing nickel ions, light scattering in the short-wave region appeared (Fig. 3, curve 3), which was indicative of the presence of inhomogeneities in solution. Nickel ions are involved in multicenter interactions with polymer chains, which decreases the solubility of the latter and causes the formation of a polymer dispersion in solution. The introduction of TUDO into the Ni/PPMA dispersion causes the appearance of a plasmon absorption peak of nickel nanoparticles (Fig. 3, curve 4) with a maximum at 395 nm. With time, this peak shifts to 464 nm (curve 5), likely because of the growth and partial aggregation of nickel particles. The introduction of TUDO into a solution containing nickel ions and PMA does not cause the reduction of nickel ions over the concentration range specified. Note that PMA molecules are also capable of coordinating nickel ions, but without dispersion formation. It follows that the reduction of nickel ions with TUDO over the concentration range studied is caused by the formation of boundaries (particles in solution and pores in the polymer).

A study of the kinetics of reduction of nickel ions in solution containing PPMA and TUDO was performed by cyclic voltammetry. TUDO and PPMA are inactive electrochemically over the potential range used. The signals of various nickel phases are unresolved in cathode dependences. In the anode region, the voltammograms of the electrolyte with nickel ions contain a peak at -0.12 V (Fig. 4, curve 2) related to the oxidation of nickel electrochemically reduced from hydrated ions. The peak at -0.4 V (Fig. 4, curve 3) appears when PPMA is added to the solution; it is related to the oxidation of nickel electrochemically reduced from ions coordinated by polymer molecules. When TUDO is introduced (Fig. 4, curve 4), an additional signal at -0.67 V appears; it corresponds to the oxidation of $\text{Ni}(0)$ particles adsorbed from solution on the surface of the electrode. The time dependence of the intensity of the last two signals passes a maximum, which can be related to a change in the effective charge on the polymer chain that coordinates metal particles and ions and the precipitation of the polymer with nickel particles.

It follows that these signals cannot be used to study the kinetics of reduction of nickel ions. The concentration of nickel ions was measured using the signal at -0.12 V . Ni^{2+} ions bound with the polymer were released after the transition of the polymer into the acid form caused by the addition of HClO_4 to the solution at a fixed time moment. Perchloric acid was selected because it did not form complexes with nickel ions and,

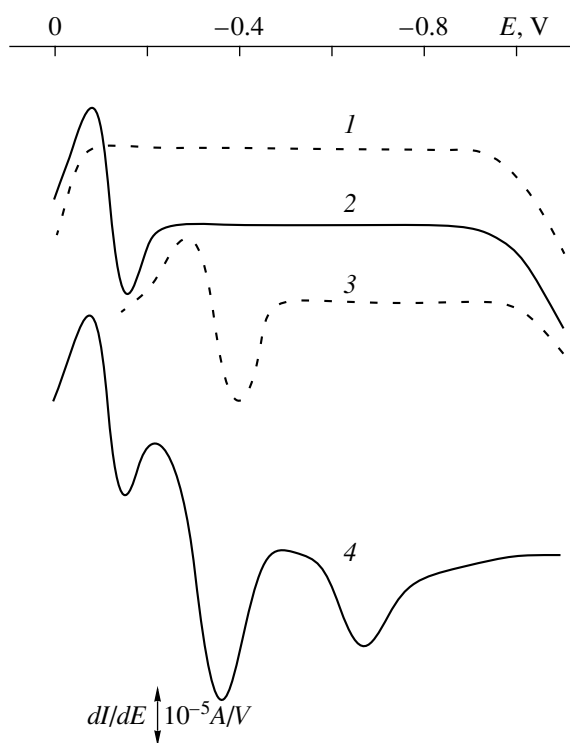


Fig. 4. Anode branches of voltammograms of (1) background electrolyte, (2) Ni^{2+} ions, (3) nickel ions in the presence of PPMA, and (4) solution containing Ni^{2+} , PPMA, and TUDO.

in dilute solutions, did not oxidize elemental nickel. Preliminary experiments showed that, in addition to the release of nickel ions, perchloric acid caused the disappearance of light scattering in solution and stopped the reduction reaction.

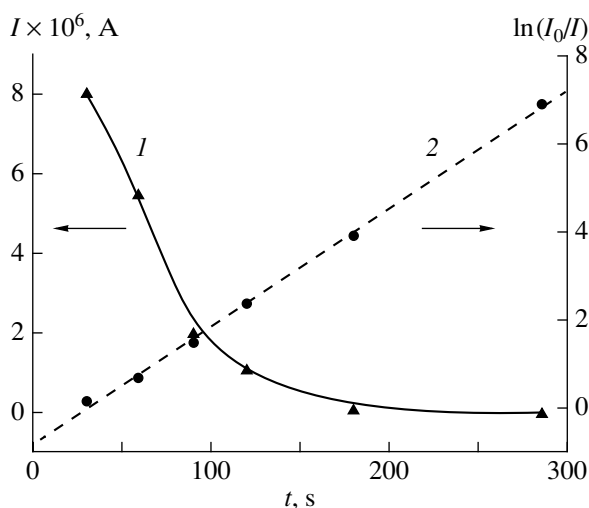


Fig. 5. (1) Time dependence of nickel oxidation current at -0.12 V after the addition of TUDO and (2) linearized form of this dependence.

The results of our kinetic studies of the reduction of nickel ions by TUDO are shown in Fig. 5. The voltammetric signal of nickel ions proportional to their concentration decreases as time passes. The dependence obtained over the range 30–300 s is well linearized in the coordinates $\ln(I_0/I)$ versus t , which is evidence of the first order of the reaction with respect to nickel ions. This corresponds to the order of the reaction in aqueous solution [16]. The rate constant for the reaction is 0.03 s^{-1} . Nuclei of nickel particles formed during the first 30 s of the reaction are unstable thermodynamically (the corresponding data are not shown in the figure), and voltammetric signals obtained up to 30 s are poorly reproducible; 30 s can be considered the induction period of the reduction of nickel ions by TUDO.

Dispersions containing nickel nanoparticles can be used to limit the intensity of high-power laser radiation to protect instruments and organs of sight from its damaging action. The initial components (nickel chloride, PPMA, and TUDO) do not have nonlinear optical properties. As ions are reduced and nickel nanoparticles are formed, we observe nonlinear transmission attenuation of intense laser radiation by solution (Fig. 6). 24 h after the addition of the reducing agent to the system containing nickel chloride and PPMA, the intensity of laser radiation decreases fivefold at $W = 150 \text{ MW/cm}^2$, which is comparable with the attenuation coefficient obtained with noble metal nanoparticles [19]. We plan to study the nonlinear transmission of nickel nanoparticles in a polyacrylate matrix.

To summarize, the reduction of nickel ions by TUDO in acryl polymer pores and solution containing water-soluble polyacrylate over the concentration range studied is localized at the interface, which can be related to a decrease in the activation barrier to nucleation because of its heterogeneous mechanism. Parti-

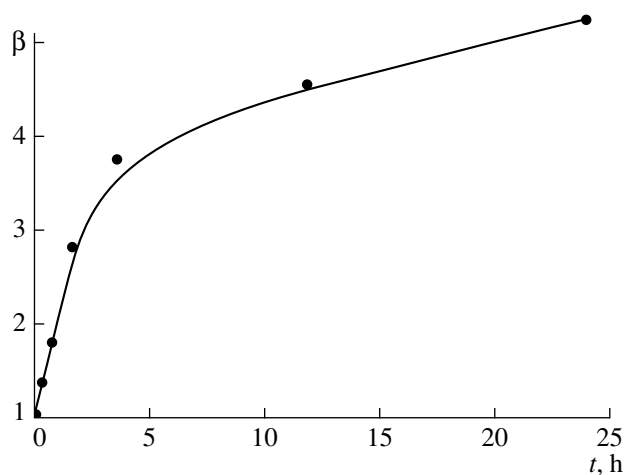


Fig. 6. Attenuation coefficient (β) of laser radiation ($W = 150 \text{ MW/cm}^2$) by a Ni^{2+} /PPMA solution at time t after the addition of TUDO.

cles anchored to the surface of pores do not experience aggregation. They only partly become agglomerated as the polymer is dried and the size of its pores decreases. This can be used to synthesize polymer composites with nanosized nickel particles inside pores. These composites containing up to ~3% metal are stable in storage, permeable to reagents when wet, and can be used to limit the intensity of high-power laser radiation.

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