TARGET SYNTHESIS OF FUNCTIONAL BIOCOMPATIBLE NANOCOMPOSITES WITH "CORE-SHELL" STRUCTURE

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Abstract. Metal-complex macroinitiators were successfully applied for the synthesis of polymer nanocomposites with core-shell structure by two-stage water dispersed polymerization. On the first stage, formation of monodispersed polymer particles of desired size and functionality is achieved by target variation of macroinitiator concentration, content of metal cations in its structure, and pH of medium. Initiation of grafted polymerization from the surface of seeded particles is provided by residual peroxide moieties of macroinitiator.

Keywords: dispersion polymerization, macroinitiators, composite polymer particles.

1. Introduction

A significant progress in biotechnology and medicine during the last years caused arising need for nanoscale composite materials with "core-shell" structure, combining desired functionality of "shell" and special physical and biological properties of "core", for their practical application as reagents for diagnostics, delivery of drugs and nucleic acids *in vitro* and *in vivo* [1, 2], as well as for visual control of processes of treatment and tissue regeneration. Controlled size and nature of "core" and "shell" functionality of polymer nano- and microcomposites determines their special physical and biological properties and, therefore, prospects of their application.

One of the most convenient approaches of tailored control of morphology and size of functional polymer nanocomposites consists in applying of surface-active initiators for their synthesis. These multi-functional initiators provide localization of radical-forming centers in specific sites of reactive system, which ensures possibility to control the kinetics of polymerization and properties of obtained polymers. It is explained by the fact that localization of initiator provides not only steric and electron control of initiation stage under some condition, but other elementary steps of polymerization as well.

First works devoted to application of multi-functional initiators for obtaining of polymer particles appeared in the 80's of the 20th century. Main principles of polymer particles formation by means of dispersed polymerization, where the oxyethylated nonionic surfactants with oxidized terminal hydroxyl moieties were used as surface-active polyperoxide initiators, were described in [3-6]. Polyethylene glycol- [7, 8] and polyacrylamide based azo-initiators [9] were used simultaneously as polymer emulsifiers and initiators of heterophase polymerization of styrene, methyl methacrylate, acrylonitrile, and vinyl acetate.

Sites of localization of radical forming centers in water dispersed polymerization system are determined by the nature of initiator. Sorption ability of surfactants has significant effect on passing and kinetics of radical reactions [10]. Commonly, kinetic peculiarities of emulsion polymerization depend on localization of polymer radical formation reactions that might occur in water phase or in micelles and monomer drops. Reactions of radical formation, located inside absorption layers of emulsifier on the surface of PMP and polymer particles, are gaining great importance due to providing control over particles formation kinetics, their morphology and surface functionality. Generation of free radicals inside absorption layers can be ensured by using of surface-active initiators for immobilization of initiating sites on the surface of PMP, as well as by adding of surfactants able to react with peroxide containing substances. The examples of such substances are alkyl pyridinium halides [11-13], able to activate decomposition of hydroperoxides, formation of free radicals, and initiation of polymerization inside formed local micellar structures in solutions or on the surface of PMP.

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Another approach to localization of free radicals formation in adsorption layers of emulsifier is based on introducing initiating centers into the structure of surfactants. It can be implemented by synthesis of surface active initiators. Combination of initiator and surfactant functions in one molecule determines the specific properties of the process of polymer particles formation due to the change of topochemistry and kinetics of water dispersed polymerization. Surface active poly- and oligoperoxides, containing hydrophobic (styrene, vinyl acetate, methyl methacrylate) and hydrophilic (maleic anhydride, acrylic acid, *N*-vinylpyrrolidone) units, were studied as surface-active initiators of water dispersed polymerization for obtaining of stable water dispersions of particles with narrow size distribution and with desired functionality [14-19]. Functionality of obtained particles surface can be regulated by change of the polymer initiator structure. The authors [20] describe the method of polymer particles formation by means of emulsion polymerization of vinyl monomers initiated by peroxidized chitosan; polymerization leads to formation of particles with polysaccharide shell.

Micro- and macrostructure, as well as molecular weight of polyperoxide surfactants determine their colloidal properties, ability to form free radicals and, respectively, kinetics and topochemistry of initiated water dispersed polymerization. The study of surface tension of water solutions of oligoperoxide surfactants, containing hydrophobic units of styrene, ditertiary peroxide moieties and hydrophilic units of maleic acid, show evidence of formation of swollen in water macromolecular globules at concentrations of 0.01 g/l [21]. It was found that their size does not depend on molecular weight of oligoperoxides and is around 0.1 nm. Swelling degree of macromolecular oligoperoxide globules depends on oligomer nature, temperature and pH of solution. However, the radius of macromolecular globule stays almost the same at different concentrations of oligomer in solution. It confirms formation of colloidal zones with size close to the size of hydrophobic moieties of single molecules in solution. Further increase of oligomer concentration in solution leads to the sharp decrease of surface tension to the minimal values, typical of micelle forming surfactants, when the radius of oligomer globules is significantly enlarged. Obviously, when the concentration of oligoperoxide reaches CCM point, oligomer globules form aggregates of several macromolecules. Emulsification of styrene in diluted water solution of oligoperoxide surfactant leads to formation of monomer drops with poorly surface adsorption [22]. Due to insufficient stability of emulsion it is separated into oil phase and water phase, containing monomer drops with saturated adsorbed stabilizing layer. According to the authors' opinion, it ensures passing of polymerization inside microdrops, stabilized by oligoperoxide surfactant, and in micellar zones, formed by surface active oligoperoxide.

In [23] obtaining of functional polystyrene particles by water dispersed polymerization, initiated by anion oligomers with *N*-tertbutylperoxymethyl acrylamide moieties is studied. As a result of water dispersed polymerization, initiated by peroxide containing surfactants, monodispersed particles with immobilized on their surface macromolecules of surfactant with residual peroxide groups, are obtained. Residual peroxides might be used for further synthesis of particles with "core-shell" structure.

Synthesis of amphiphilic polyperoxide, product of tertbutylperoxymethanol acylation by copolymer of octene and maleic anhydride, and its application as initiator of emulsion polymerization is described [24].

Authors [25] studied water dispersed ATRP of methyl methacrylate with novel commercially available oligomer disodium4-(10-(2-bromo-2-methylpropano-yloxy)decyloxy)-4-oxo-2-sulfonatebutanoate used as initiator and proved its effectiveness as stabilizer for polymer particles dispersions, as well as modifier of their surface. Different routes of polymer particles formation with complex morphology (including particles with hollow structure) are described [26] using "living" radical precipitation polymerization. The advantage of this method of polymer particles formation consists in localization of active sites (that can be used for further modification) on the surface of particles when, for example, halogen contained monomers are used. Moreover, polymerization is occurring at the absence of additional stabilizer.

Functionalization of particle surface is commonly achieved by applying of two-stage water dispersed polymerization that ensures formation of particles with "core-shell". Okubo and [27] published the results of two-stage polymerization of monomers with different polarity and showed the influence of synthesis conditions on obtained polymer particle morphology, *e.g.* "core-shell", "raspberry-like" or hollow structure type, due to phase separation of thermodynamically incompatible polymers. Morphology of particles is determined by order and method of monomers adding, as well as by hydrophilic properties of polymer. Particles with "raspberry-like" surface morphology are formed when polymerization of more hydrophobic monomer as compared to seeded particles occurs. When the polar monomer is used on the second stage of synthesis, particles with "core-shell" structure are obtained [28-31]. In [32] authors described the method of particles formation with polymethyl-methacrylate "core" and nonpolar polystyrene "shell", prepared by continuous adding of styrene with constant rate on the second stage of polymerizarion at the

temperature just few degrees below the glass transition point of polymethylmethacrylate. According to the publications [33-36], where different methods of particles preparation of "core-shell" structure with controlled morphology and size are analyzed, uniform polymer shell formation on the particle surface occurs when the swelling of seeded particles in monomer is ensured. With this regard, crosslinked particles, like copolymers of styrene and divinylbenzene, are used as seeds. Correlation analysis of particles swelling rate and their growth during seeded polymerization at the absence of emulsifier, allowed Wilkinson and coauthors [37] to make a conclusion that probability of particles growth due to adsorption of monomer is negligible. They also suggested that flocculation of seeded and overcoated particles, poorly stabilized due to swelling in monomer at the absence of surfactants. Effect of stabilizing effectiveness of styrene and acrylic acid copolymer on proceeding of elemental stages of water dispersed polymerization of styrene is studied [38]. It is shown [38, 39] that stabilizer forms highly viscous zones around the particles and it leads to decreasing diffusion rates of monomer and oligomer radicals inside PMP and restriction desorption of radicals from particles surface.

Method of submicron dimensioned particles preparation is investigated by polymerization of vinyl monomers at the absence of emulsifier with further application of obtained particles for seeded polymerization [40-43]. The main drawback of this method is broad size distribution of particles because of formation of new seeds on the second polymerization step. To prevent formation of new particles during seeded polymerization, method of "active" swelling with following polymerization of monomer in swollen particle is proposed [43-46]. Principal feature of this method is that oligomers with very weak water solubility but high monomers solubility, polymerized on the second stage, are used as seed particles. Another method called "dynamic" swelling, quite similar to the previous one, is used to prepare near micron-sized particles [47-51], where monomer was highly adsorbed on the surface of seeded polymer particles from its alcohol solution at constant slow addition of water due to reducing its solubility in mixed solvent. This method gives the opportunity to obtain complex shaped particles (disk-like or polyhedral) [52].

In [53-55] new approach of composite particles with "core-shell" structure is proposed, according to which the polyperoxide emulsifier, immobilized on the surface of seed polymer particles, is used. Grafting of emulsifier to the particles, occurred due to decomposition of peroxide groups, provides localization of initiation of polymerization on the second stage and formation of polymer shell on the surface of latexes. Authors suggested that this method of composite particles formation

promotes improvement of compatibility of water polymer dispersion components, loaded polymer systems, and polymer mixtures. In [56] the possibility to form hollow microsphere particles by neutralization of carboxyl groups, localized inside the polar "core" of polymer particles with "core-shell" structure is shown. These polymer particles with polar "core" and styrene copolymer based "shell" are synthetized by grafting polymerization, initiated from the surface of polymethacrylate particles, modified with functional polyperoxides.

Submicron-sized particles with unique multilayered morphology are synthetized by two-stage ATRP in water medium. On the first stage, miniemulsion ATRP procedure is used to synthetize polyisobutylmethacrylate particles containing bromine atoms in the structure of molecules. On the second stage, previously obtained polymer particles serve as seeds and components of initiation system [57, 58]. Method of ATRP allows to obtain particles with crosslinked "core" and polymer "shell" formed from different monomers. Localization of radical forming sites on the surface of particles on the first stage is ensured by introducing of bromine- contained monomer 2-methacryloxyethyl-2′-bromoisobutyrate to the structure of polymer core [59].

Thus, possibility of synthesis compatible polymer composites with controlled functionalization and reactivity are the main driving forces that make them more and more attractive material for analytical cellular labels, like magnetic or luminescent ones, for *in vitro* and *in vivo* detection, as well as carriers for target drug delivery [60-66]. Capsulation of fluorescent dyes is a promising method of luminescent nanocomposites with "core-shell" structure formation providing controlled content of dye inside the core of polymer particles, desired brightness, reliable protection against leakage and bleaching under UV-irradiation.

In this work, we analyze the results of tailored synthesis of functional polymer particles with "core-shell" structure by step-by-step polymerization, initiated by oligoperoxide metal complexes (OMC) that also served as macroinitiator with different thermal stability of peroxide moieties.

2. Experimental

2.1. Reagents and Materials

Monomers: styrene (St) (Merck), methyl methacrylate (MMA) (Acros), *N*-vinyl pyrrolidone (NVP) (Merck), glycidyl methacrylate (GMA) (Merck), vinyl acetate (VA) (Merck), butyl acrylate (BA) (Merck), butyl methacrylate (BMA) (Acros), and acrylic acid (AA) (Fluka) were additionally purified by vacuum distillation

or distillation column, after which their characteristics became close to the ones described in literature data [67]. Maleic aldehyde (MA) was purified by vacuum sublimation; temperature of melting after purification was 325 K ($T_m = 325.9$ K [68]). Surface-active monomer triethyl ammonium 3[(Z)-4-cetyloxy-4-oxy-2-butenoil-oxy]-1-propylsulfonate (SAM) and peroxide containing monomer 2-tert-butylperoxy-2-methyl-5-hexen-3-yne (VEP) were synthesized according to techniques described earlier [69] and [70], respectively. After purification VEP was characterized by the following parameters: [O] = 8.7 %, $d_4^{20} = 867$ kg/m^3, $n_d^{20} = 1.4482$.

Emulsifier – sodium pentadecyl sulfate (PSS) (ABCR GmbH & Co. KG) – $C_{15}H_{31}SO_3Na$, (CCM = 0.037 %, $\sigma_{CCM} = 34$ mN/m [71]).

Surface-active oligoperoxide metal complex initiator (OMC), whose general structure is shown below, was synthesized according to techniques described earlier [72].
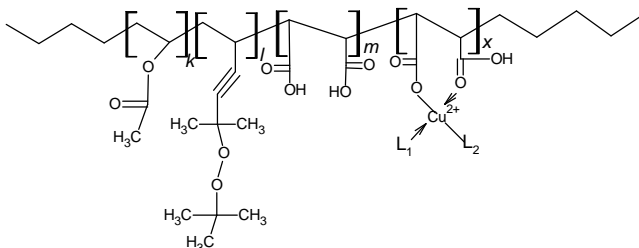
$k = 22$ %; $l = 34$ %; $m = 42$ %; $x = 2$ %; $Mn \sim 2000$ g/mol, we used OMC with a different content of Cu(2+)
$[Cu^{2+}]_{OMC} = 0.4, 0.6, 0.85, 1.1$ % L_1, L_2 – low-molecular weight ligands, like water or alcohol

Functional oligoperoxides (FO) that were used as ligands for OMC obtaining, were synthesized according to technique described earlier [73]. FO were obtained by copolymerization of VA, VEP, and MA (molar ratio – 22.8:32.2:45.0) at 333 K in ethyl acetate, 2,2′-azobis (2-methylpropionitrile) (AIBN) was used as initiator. Synthesis of OMC was conducted in the following way: 10 % solution of FO and 5 % solution of CuCl$_2$ in ethanol was mixed and stirred for 30 min at 298 K. When the stirring was finished, the reactive mixture was precipitated in distilled water. OMC was thoroughly purified from residual salt with further drying under vacuum. Content of metal cations was measured by element analysis and atom-adsorption spectroscopy.

Dyes: fluorescent dye fluorescein (Aldrich) ($l_{ex} = 494$ nm, $l_{em} = 521$ nm); fluorescent dye 2,6-di-*tert*-butyl-4-(2,5-diphenyl-3,4-dihydro-2H-pirazole-3-yne)-phenol (pyrazoline)* ($l_{ex} = 366$ nm, $l_{em} = 445$ nm) (synthesized according to the method described in [74]).

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* Dye was synthesized by assistant professor of Department of Technology of Biologically Active Substances, Pharmacy and Biotechnology Ph.D. Semen Khomyak

2.2. Synthesis of Polymer Particles *via* Water Dispersed Polymerization

Polymer particles were obtained *via* water dispersed (emulsion) polymerization method. Polymerization was carried out in glass reactor equipped with thermostat, stirrer and condenser. Water phase for emulsion polymerization was previously distilled, boiled for 15 min to remove oxygen and purged with argon; pH of water medium was adjusted to 9 by adding certain amount of 25% solution of ammonium. Initiator-stabilizer OMC and sodium pentadecyl sulfate, when polymerization was conducted in the presence of additional emulsifier, were dissolved in water phase. When polymer particles with SAM were obtained, the last one was dissolved in oil phase. After complete dissolving of OMC in water, monomers were added to it and stirred. The residual monomers after polymerization were removed by vacuum drying of obtained dispersions at 323 K.

2.3. Synthesis of Polymer Particles with "Core-Shell" Structure

Polymerization was carried out in hermetic sectional dilatometers hermetically with stirring. Water dispersions of polymer particles, synthesized in presence of OMC, were used as initiators for conducting of seed polymerization. Water dispersions were purified by dialysis before polymerization step. Water dispersion of polymer particles and monomers were loaded in dilatometer without any additional initiators used. After loading all components, dilatometer was cooled, vacuumed and purged with argon. Polymerization was carried out at 313 K.

2.4. Synthesis of Polymer Particles with Capsulated Luminescent Dyes in the Core

Obtaining of nanocomposite particles with "core-shell" structure and simultaneous *in situ* capsulation of luminescent dyes were carried out in the following way: certain amount of fluorescent dye was dissolved in monomer mixture St:SAM or TSM; OMC was dissolved in 1.25 % ammonium water solution, pH of the obtained solution was adjusted to 8 by dropwise addition of 5 % ammonium water solution; solution of dye in monomer and aqueous ammonia solution of OMC were loaded in reactor with stirrer (or in sectional emulsion dilatometer), purged with argon and stirred at 313–323 K. Formation of functional shell of tailored nature on the surface of particles occurred *via* seed polymerization method, where synthesized particles with dye in the core and peroxide

groups on the surface served as seeds. Water dispersions were purified by dialysis before polymerization step. Polymerization was initiated by residual peroxide moieties of OMC on the surface of particles.

2.5. Kinetic Study of Polymerization

Conversion of monomers (*S*) was determined using dilatometric method according to the formula [75]:

$$S = \frac{\Delta V}{V \cdot k} \cdot 100\,\% \qquad (1)$$

where *V* – initial volume of monomer at certain temperature, ml; ΔV – change of volume of polymerization system over the time, ml; *k* – average contraction coefficient for used monomers at temperature of polymerization [76]. Polymerization rate R_p (%/s) was determined by tangent to the curve of *S = f(t)* dependence on the stationary section and recalculated in $mol \cdot l^{-1} \cdot s^{-1}$ units [75]. Deviation of polymerization rate determined in parallel experiments was 5–7. Gravimetric method also was used for control of dilatometric measurements of water dispersed polymerization [75]. Effective rate constant of polymerization R_p ($mol \cdot l^{-1} \cdot s^{-1}$) was calculated from the equation [75]:

$$R_p = k_{ef} \cdot [I]^n \cdot [M]^b \qquad (2)$$

2.6. Analysis Techniques

Methods of element analysis and potentiometric titration were used to determine the amount of functional moieties in copolymer chains and on the surface of nanoparticles [77].

Sizes of nanoparticles were measured by light scattering method with photo colorimeter LMF-72M [78], dynamic light scattering (DLS) with Zetasizer Nano ZSP (Malvern Instruments Ltd, United Kingdom of GB), and transmission electron microscopy (TEM) with electron microscope JEM-200A (JEOL, Japan).

IR-spectra of adsorbed layer were performed at Tensor-27" (Bruker) with diffuse reflection supply Specac "Selector" in the range of 500–4000 cm^{-1}. Spectra of luminescence were registered by automatic spectral device. To excite the luminescence hydrogen lamp with the wavelength of $\lambda = 260$ nm was used, narrowed by monochromator MDR-2. Analyzed samples were placed in transparent quartz cuvettes. The luminescence irradiation of the sample reached the monochromator MDR-12. Registration of irradiation was performed by photo multiplier FEU-100 and corresponding signal was registered on PC. The dynamic viscosity of the polymer dispersions were measured by RHEOTEST 2,1 (Germany) under different shear rates (*cone-plate device*), at 298±0.05 K [78] .

3. Results and Discussion

As was shown earlier [79], ditertiary peroxide moieties of OMC surfactants form free radicals in alkaline water solutions in wide temperature range that determines the possibility of their application as multi-site initiators of radical polymerization in water solutions and dispersions at comparatively low temperature (273–298 K) and provides obtaining of polymer particles with desired size and functionality, as well as molecular-weight polymer characteristics.
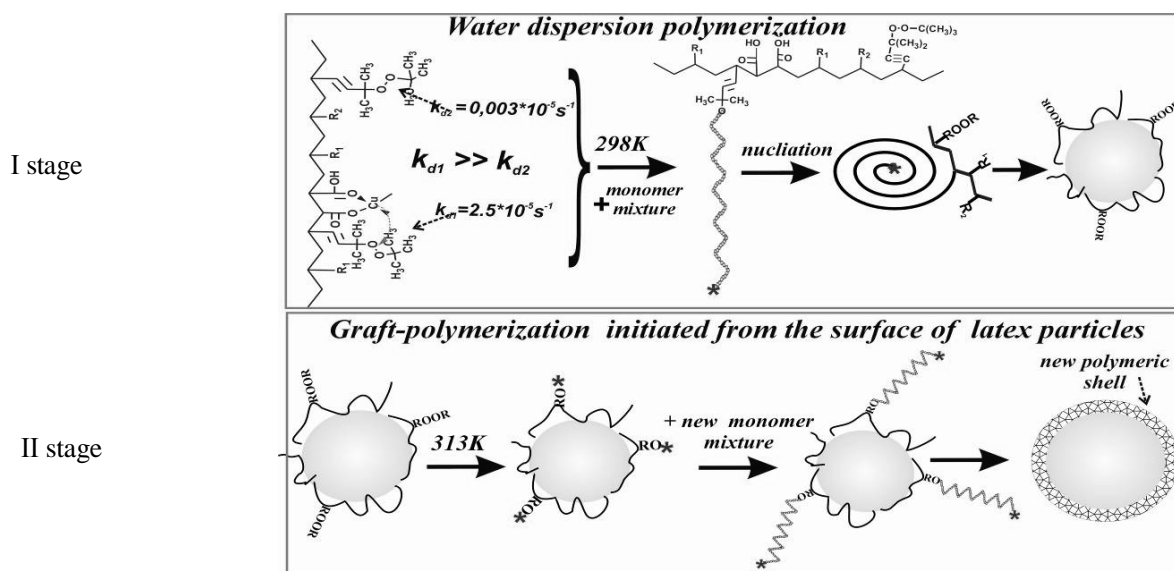

Fig. 1. Scheme of obtaining nanocomposites with "core-shell" structure
via two-stage water dispersed polymerization, initiated by OMC

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Characteristics of emulsion polymerization of different monomers, initiated by OMC
(pH = 9; 298 К; H₂O:monomer = 5:1)

Emulsifier-initiator	Monomer	$[\text{initiator}]^* \cdot 10^2$, mol/l	$R_p \cdot 10^4$, mol/l·s	$k_{ef} \cdot 10^2$, l·mol·s^{-1}	Order of OMC
OMC, ligand oligo(VA-co-VEP-co-MA), $[Cu^{2+}]$ = 0.4 %	St	1.95	3.0	0.47	0.70
		3.9	4.5		
		7.9	8.0		
	BMA	3.9	2.0	0.55	1.00
		7.9	5.0		
		15.8	9.0		
	MMA	3.9	1.2	0.63	1.20
		7.9	2.0		
		15.8	7.0		
OMK, ligand oligo(VA-co-VEP-co-MA), $[Cu^{2+}]$ = 0.85 %	St	0.76	1.5	0.74	0.75
		3.9	7.8		
		7.9	15.0		
		59.3	40.0		
	BMA	3.9	7.9	2.1	1.06
		7.9	18.0		
		15.8	32.0		
	MMA	3.9	8.0	4.3	1.22
		7.9	29.0		
		15.8	42.0		

It was found that only 25–30 % of ditertiary peroxide moieties form free radicals at reduced temperature, whereas the others are introduced into the structure of polymers mainly as a part of OMC molecules, localized on the surface of polymer nanoparticles formed *via* water dispersion polymerization. It determines the role of OMC multi-site initiators that can serve as functional polyperoxides**,** containing peroxide moieties with different thermal stability capable to form free radicals and initiate polymerization at different temperatures. Thus, we developed new approaches for synthesis of functional nano- and microcomposites with "core-shell" structure *via* two-stage water dispersed polymerization, initiated by OMC- pemosors in different temperature range, according to the scheme (Fig. 1).

As can be seen from Fig. 1, the first stage of polymerization leads to formation of polymer nanoparticles with surface ditertiary peroxide moieties that are structural components of obtained polymer molecules. Peculiarities of synthesis of described peroxide precursors for synthesis of functional polymer composites with "core-shell" structure are discussed below.

3.1. Synthesis and Properties of Peroxide-Contained Polystyrene and Polyacrylate Nanoparticles

It is known [79] that water soluble OMC are not effective surfactants. However, application of OMC molecules as initiators of polymerization provides formation and stabilization of polymer dispersions without additional emulsifiers and initiators. OMC are effective low-temperature initiators of water dispersed polymerization of different monomers. Dependences of rates and effective rate constants of polymerization for different monomers are determined by the content of OMC in initiating system (Table 1). Effective rate constants of polymerization rise with increasing of content of Cu^{2+} cations in OMC increase in the order: St<BMA<MMA.

It might be explained with increasing ability of monomers in the mentioned order to coordinate on cationic OMC and thus rising of polymerization rate constant. Reducing the content of coordinating centers in water phase with lowering of OMC concentration leads to decrease of effectiveness, rate of initiating and, consequently, of the amount of PMP in system, that defines the general polymerization rate.

This assumption is confirmed by obtained dependences of size and, respectively, amount of PMP on the content of OMC in the system (Fig. 2). Although for styrene there is no essential dependence of particles size on OMC content in solution in the studied range, the size of particles obtained in case of BMA and MMA polymerization significantly decreases and their amount increases with the growth of OMC content.

It was shown earlier [17, 79] that the value of pH in solution of OMC has influence on their colloidal properties and rate of radicals formation, which, in its turn, determines the topochemistry and kinetics of water dispersed polymerization initiated by OMC (Fig. 3a). Increasing pH values of OMC solutions results in
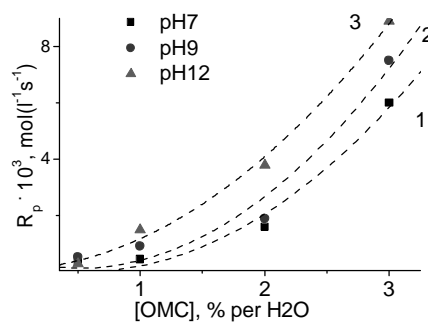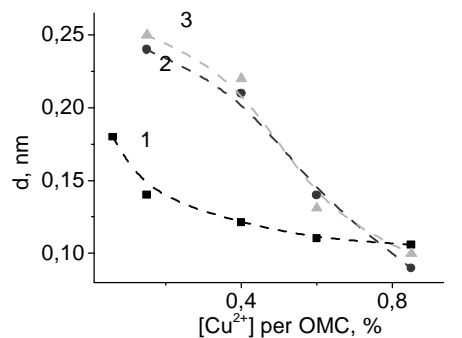
acceleration of polymerization rate of St initiated by OMC, which is explained by increased rate of free radicals formation and rate of polymerization initiation (Fig. 3b).

Fig. 2. Dependences of polymer particles size in water dispersions, obtained *via* polymerization of styrene (1); butylmethacrylate (2) and metylmethacrylate (3) initiated by OMC on content of Cu^{2+} in OMC
([OMC]$_{per\ monomer}$ = 3 %, pH = 9, 298K; H_2O: monomer =5:1)
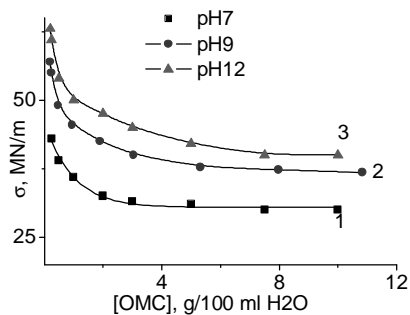
a)

b)

Fig. 3. Surface tension isotherms of OMC water solutions (a) and dependence of water dispersed polymerization rate of St on OMC concentration (b) at different pH values: 7.5 (1); 9.0 (2) and 12.0 (3). *T* = 298 K, [Cu^{2+}]$_{in\ OMC}$ = 0.85 %

[OMC] = 0.5 % per H_2O

a)

b)

c)

[OMC] = 2.0 % per H_2O

d)

e)

f)
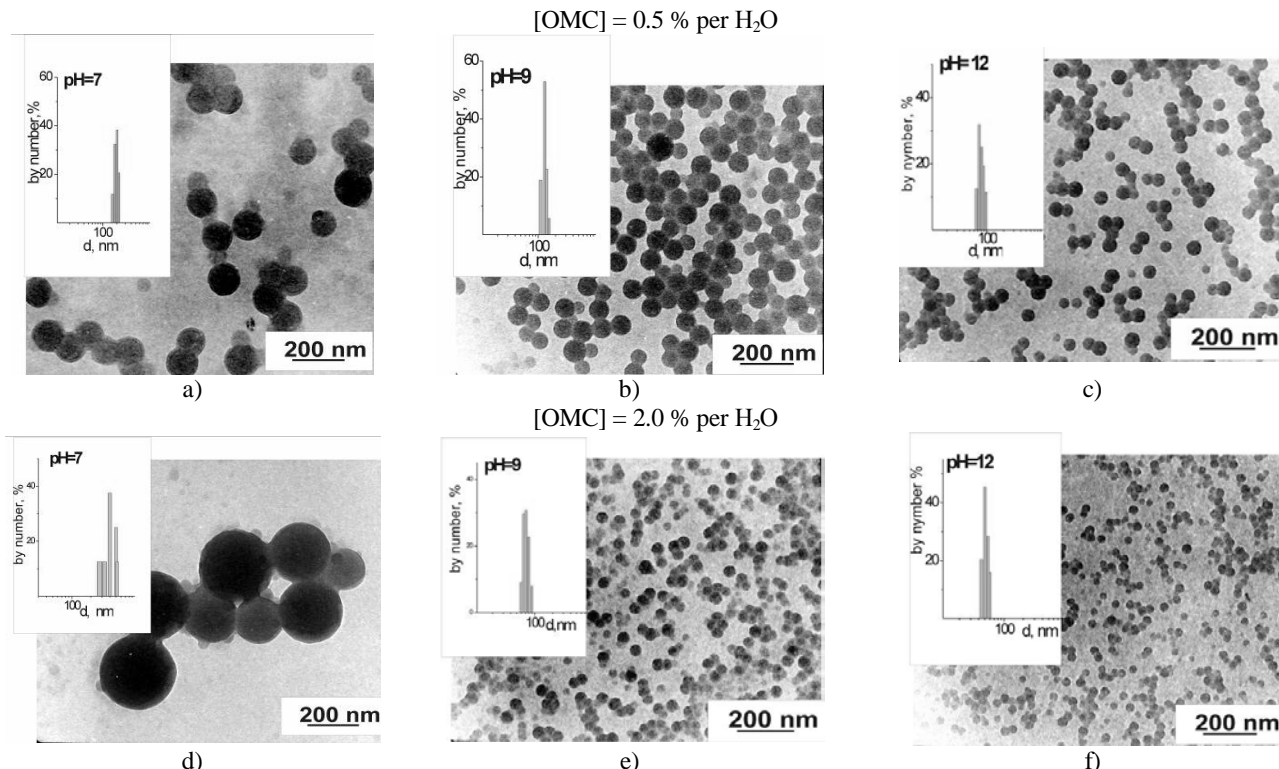
Fig. 4. TEM images of polystyrene nanoparticles obtained *via* water dispersed polymerization, initiated by OMC, [OMC] = 0.5 % (a, b, c) and 2 % (d, e, f) in water phase at different pH values: 7 (a, d), 9 (b, e) and 12 (c, f) (histograms of polystyrene nanoparticles size distribution are shown on the insets)

Increasing the rate of polymerization initiation and, respectively, amount of formed PMP, at increasing the values of pH leads to decreasing of the size of obtained polymer particles (Fig. 4). Increasing effectiveness of OMC molecules grafting to polystyrene particles with the growth of pH values, results in preventing of their aggregation during polymerization.

Molecular weight of polymers also increase with growth of pH values as a result of decreasing of termination rate constant of polystyrene chains in PMP (k_0^{pH7} = 832 l/mol·s; k_0^{pH9} = 300 l/mol·s; k_0^{pH12} = 50 l/mol·s), where the polymerization elementary stages take place (Fig. 5).
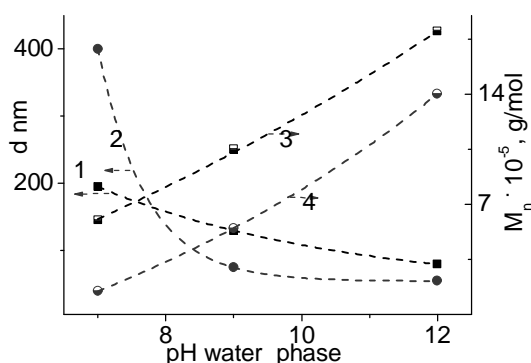
Fig. 5. Dependences of particles size (1, 2) and molecular weight (3, 4) of polystyrene on pH values of solutions during water dispersed polymerization, initiated by OMC ([OMC] = 0.5 wt % (1, 3) and 2 wt % (2, 4) in water phase, ratio St:H$_2$O = 1:5; 298 K, $[Cu^{2+}]_{in\,OMC}$ = 0.85 %
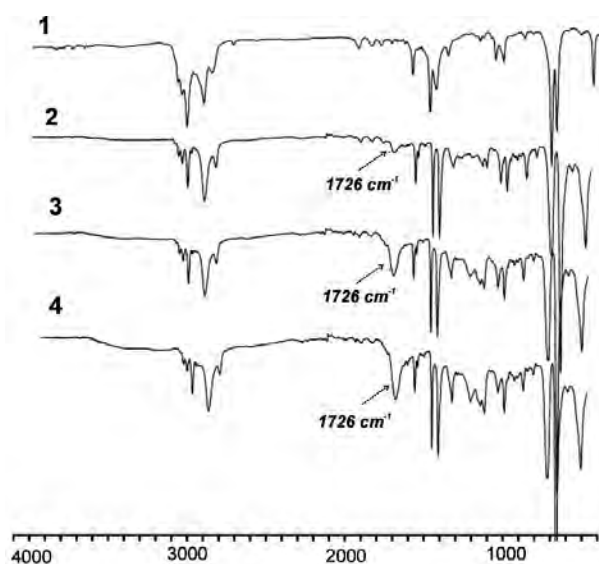

Fig. 6. IR-spectra of polystyrene nanoparticles obtained in the presence of ammonium persulfate (1) (spectrum from Aldrich database) and 2 % of OMC ($[Cu^{2+}]_{in\,OMC}$ =0,85 %) in H$_2$O at different pH values: 7.5 (2); 9.0 (3) and 12.5 (4)

Growth of pH values of reactive system leads to increasing of amount of OMC molecules, grafted to the polystyrene nanoparticles surface. As it can be seen from the IR-spectra of polymers (Fig. 5), intensity of band, corresponding to C=O stretching vibration (1760 cm^{-1}), increase with the growth of pH, which confirms conclusions about higher rates of radicals formation, including oligomeric ones, as a result of OMC decomposition in alkaline medium.

3.2. Synthesis and Properties of Peroxide contained Poly(Styrene-co-Monomer Surfactant) Nanoparticles

Localization of initiation stage during water dispersed polymerization, *i.e.* structure and properties of initiator, is of principal importance for obtaining functional nanoparticles. Comparative analysis of obtaining water dispersions of polymer nanoparticles *via* copolymerization of styrene with surface-active monomer (SAM), initiated by different initiators, like water soluble ammonium persulfate (AP), water insoluble azobis (2-methylpropionitrile) (AIBN), and water soluble OMC surfactant, evidence crucial role of initiator nature that determine not only kinetics of polymerization in the presence of SAM, but also mechanism of formation and stabilization of functional polymer particles. At the same time, high surface activity of SAM [80] and its solubility in water and nonpolar organic media facilitate possibility of formation and stabilization of water emulsions of water insoluble monomers and determine the topochemistry and kinetics of their polymerization in the presence of SAM, as monomer and stabilizer simultaneously, and, thus, the structure of obtained polymer nanoparticles. The size of the particles (Fig. 7) obtained *via* water dispersed polymerization initiated by different initiators indicates the formation of poly(St-co-SAM) nanoparticles dispersion by various mechanisms, that determine their size and stability of dispersions. Formation of monodispersed particles with small size, independence of particles size on conversion, and their stability against aggregation during polymerization, initiated by OMC surfactant, even when concentration of SAM is only 0.5 wt %, are peculiar features of the mechanism of nanoparticles nucleation in OMC solutions. Stable water dispersions of unimodal nanoparticles with the size 85 nm are obtained by polymerization initiated by OMC. Polymerization initiated by liposoluble AIBN provides formation of more monodispersed particles, as compared to procedures where water-soluble AP is an initiator (Fig. 8).

Obviously, mechanism and topochemistry of PMP formation during polymerization initiated by initiators of different nature determine the structure and density of packing of stabilizing adsorption layers on PMP and

polymer particles and, respectively, stability of their water dispersion. The most effective mechanism of nanoparticles stabilization, obtained *via* polymerization, initiated by surfactant OMC macroinitiator, involves predominant localization of polymerization process on the surface of PMP and consequent formation of tightly packed hydrophilic layer of OMC-graft-poly(St-co-SAM) molecules.

3.3. Functional Polymer Nanocomposites with "Core-Shell" Structure

Study of polymerization initiated from the surface of polySt particles of different size with equal content of peroxide moieties shows that the number of particles is a crucial parameter that determines the rate of polymer formation (Fig. 9) and new particles are not formed during polymerization in the system. Independence of seed polymerization rate from E-30 concentration and its dependence on the content of primary particles-initiators (seed particles) in water dispersion (Fig. 9) evidence proceeding of polymerization entirely on the surface of seeds (seed particles), which provides grafting of polymer shell and increasing of particle size and functionality of particle surface (Fig. 10).

As it can be seen (Fig. 9), polymerization rate increases with increasing content of particles with adsorbed OMC on the surface, even at steady total concentration of VEP units. The same dependences of polymerization rate on size, i.e. number of particles, are observed during seed polymerization, leading to grafting of polymer shell formed from poly(NVP-co-GMA) chains, to the surface of polySt particles.

IR-spectra of primary polySt and composite particles with polySt core and poly(NVP-co-GMA) shell contain absorption bands at 1580, 1450 and 720 cm^{-1}, that correspond to vibration of aromatic rings of polySt. The presence of bands at 1720 cm^{-1}, attributed to stretching vibrations of C=O groups in the spectra of particles, is caused by grafting of OMC molecules containing units of

vinyl acetate and maleic acid. Grafting of functional shell to the surface of polySt particles is confirmed by appearance of bands at 1650 and 1460 cm^{-1}, that correspond to stretching vibrations of –N–C=O moieties of *N*-vinylpyrrolidone and deformation vibration of methacrylate –CH$_3$ group, respectively. A set of signals at 1200–1100 cm^{-1} in the spectra of composite particles is assigned to vibration of epoxide group of GMA [81].

Grafting of functional polymer shell containing NVP units to the surface of particles during polymerization is also confirmed by elemental analysis (Table 2).

The study of rheological properties of water dispersion of particles before and after polymerization also evidences the change of functionality of nanoparticles due to polymer chains grafting to their surface. Water dispersion of composite particles with polySt core and poly(MMA-coBMA-coAA) shell are characterized by dilatation, which is not observed for polySt particles (Fig. 11). It was shown that different peroxide containing nanoparticles and monomers can be applied for obtaining multilayered functional nanocomposites with "core-shell" structure by means of polymerization, initiated from the surface of particles with covalently bound moieties of OMC molecules.
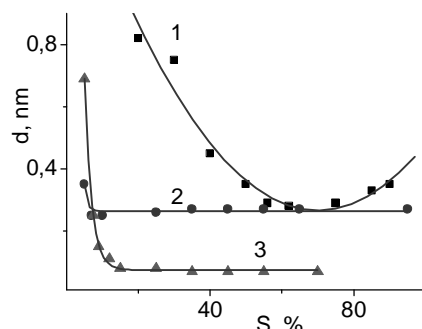

Fig. 7. Dependences of particles size on conversion of water dispersed copolymerization of St:SAM initiated by ammonium persulfate (1), azobis(2-methylpropionitrile) (2), and OMC (3) ([Cu^{2+}]$_{in OMC}$ = 0.85 %); ([initiator]=10%$_{mol}$ on monomers)
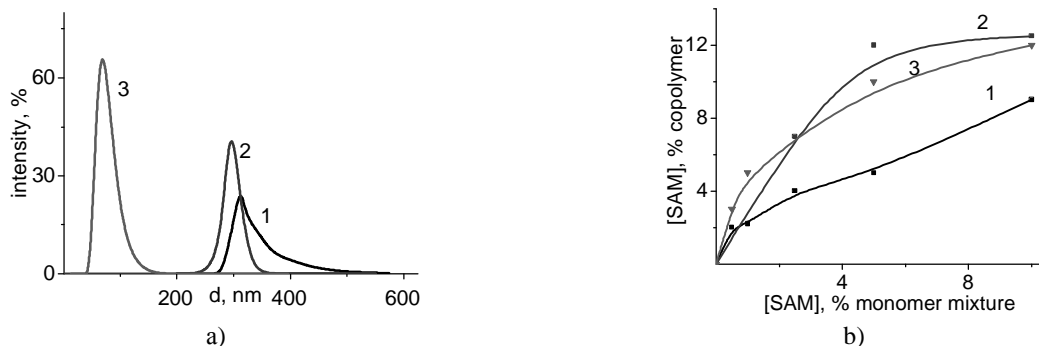

a)

b)

Fig. 8. Size distribution of particles obtained *via* emulsion copolymerization of styrene and SAM (90:10 mol %) (a) and dependence of content of monomer surfactant units in copolymer chain on its concentration in monomer mixture, when ammonium persulfate (1), azobis(2-methylpropionitrile) (2), and OMC ([Cu^{2+}]$_{in OMC}$ = 0.85 %) (3) are used as initiators of polymerization (b) (T_{pol} = 323 (1), 333 (2) and 298 K (3), [initiator] = 10 mol % on monomers)
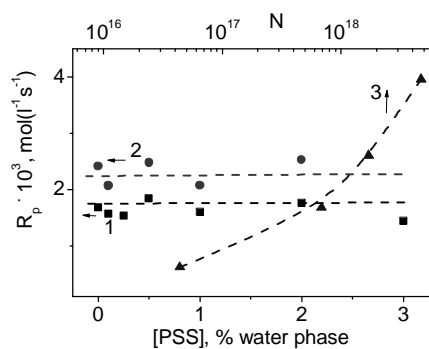
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Fig. 9. Dependence of seed polymerization rate of styrene (1, 3) and methyl methacrylate (2) on the content of PSS (emulsifier) and amount of seed particles (N) ([VEP] = $6.0\pm0.5\cdot10^{-2}$ mol/l, pH = 11, T = 318 K)
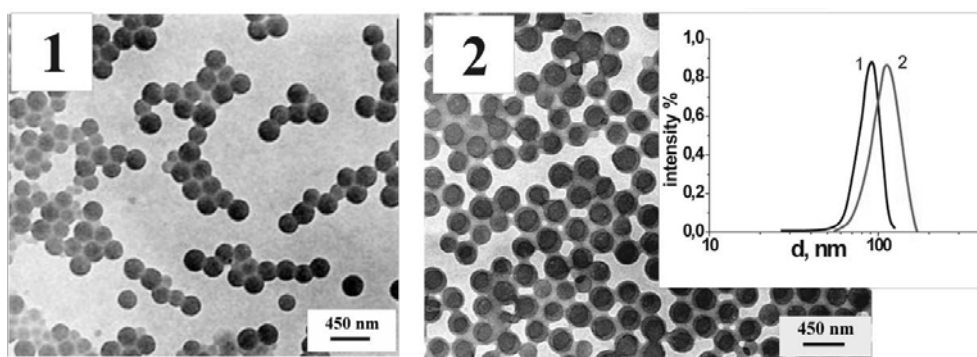

Fig. 10. TEM images of polystyrene particles in water dispersions obtained by bypolymerization initiated by OMC ([OMC] = 2 %, pH = 9, T = 298 K) (1) and particles with "core-shell" structure obtained via seed polymerization of styrene initiated from the surface of dispersed polystyrene particles (where polystyrene serves as "core" and copolymer of N-VP and GMA – as "shell") (2). Histograms of particles size distribution are shown on the insets
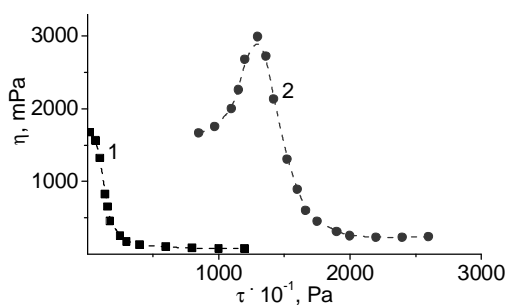

Fig. 11. Dependences of dynamic viscosity of polystyrene water dispersion (1) and dispersion of particles with polystyrene "core" and poly(MMA-coBMA-co-AA) "shell" (2) (content of polymer in dispersion is 22 wt %)

Table 2

Characteristics of polySt nanoparticles with poly(NVP-co-GMA) shell, obtained *via* seed polymerization method (70:30 mol %)

First stage					Second stage[*]		
Content of OMC, % on monomer	pH during synthesis	Size of particles, nm	Content of polymer in water dispersion, %	Content of VEP units in oligoperoxide, drafted to polymer "core", %	Content of nitrogen in particles, %	Content of polymer "shell" relative to polymer "core", %	Size of particles, nm
10	7	205	17	0.98	0.75	11.0	260
10	9	81	17	2.00	1.50	20.0	100
10	11	62	17	2.05	1.61	23.0	78
10	12	45	17	1.85	1.25	18.8	60

Note: * [monomers on second stage] = 25 % to seed particles

3.4. Functional Nanocomposites with Luminescent Dye in their Core

Two stage copolymerization of styrene, surface-active monomer and dyes initiated by OMC, with simultaneous *in situ* capsulation of dyes, is used to synthesize functional monodispersed nanoparticles with luminophores localized in their core and safely protected from leakage and bleaching (Fig. 12).

SAM and OMC are key components of the system, providing target synthesis of nanocomposites with fluo-rescent dyes in core and functional shell. Study of kinetic dependences of styrene and SAM conversion in water dispersed polymerization in the presence of pyrazolone (PRZ) and fluorescein (FL) in monomer mixture shows that increasing of dyes content leads to decreasing of polymerization rate and growth in the size of the obtained particles (Fig. 13).

It might be caused by interaction of dye molecules in chain transfer reactions, which results in the formation of low-active radicals and leads, therefore, to decrease of PMP amount and growth of their size.
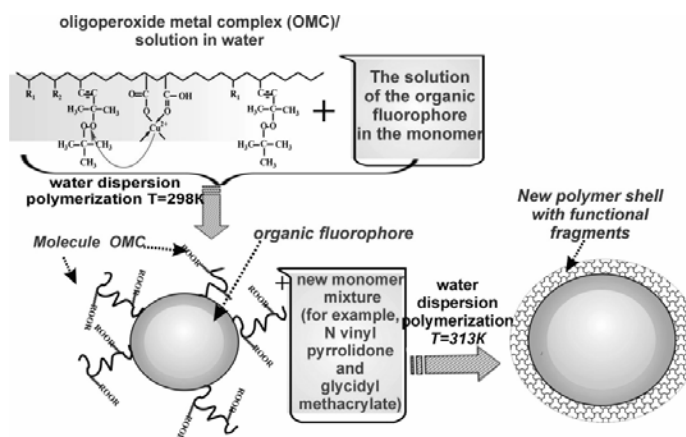
Fig. 12. Scheme of luminescent nanocomposite particles formation

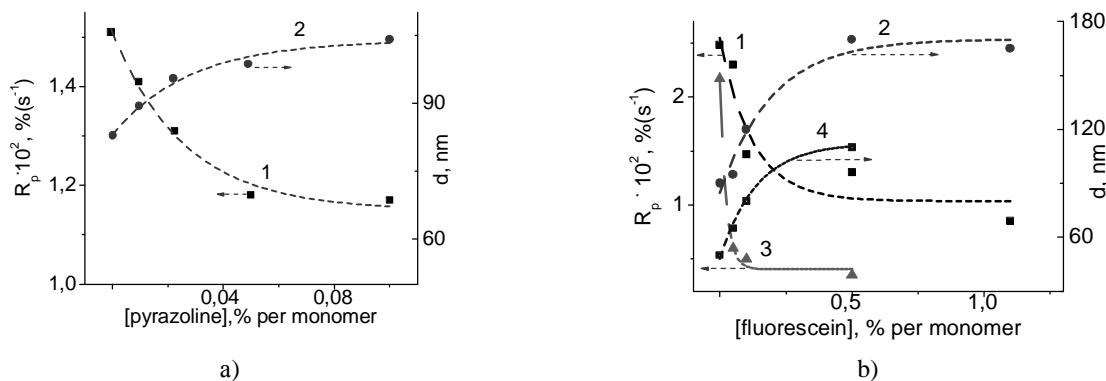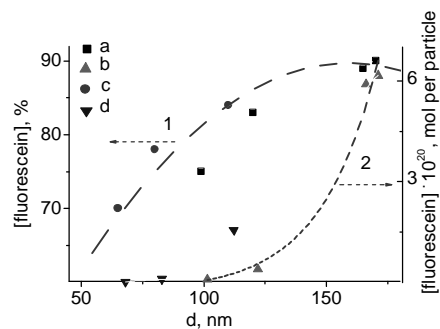a)   b)

Fig. 13. Dependences of copolymerization rates of styrene and surface-active monomer (90:10 mol %) (1), styrene, butyl acrylate, glycidyl methacrylate and surface-active monomer (65:15:10:10 mol %) (3) and particles size of water dispersions of styrene and surface-active monomer copolymer (2) and styrene, butyl acrylate, glycidyl methacrylate and surface-active monomer (4) on concentration of pyrazoline (a) and fluorescein (b)

Fig. 14. Dependence of fluorescein content (FL) inside nanoparticles after washing (% on initial content of FL) (1) and total content of fluorescein per one nanoparticle on its size (2) (a, b – mixture of styrene and surface-active monomer; c, d – mixture of styrene, butyl acrylate, glycidyl methacrylate and surface-active monomer, initiator – OMC)
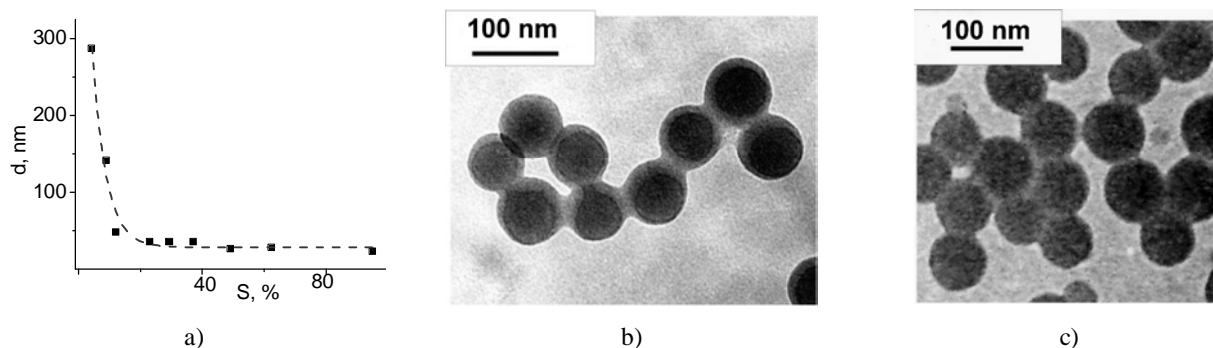
a)   b)   c)

Fig. 15. Dependences of nanocomposite size on conversion of styrene during water dispersed polymerization initiated by OMC ([SAM] = 10 % on St, phase ratio = 1:5, 298 K) (a) and TEM images of polymer nanocomposites synthesized *via* water dispersed copolymerization of styrene and surface-active monomer with different initial content of FL (molar ratio St:SAM = 90:10 mol, initiator – OMC:[FL] = 0.05 % on St (b), [FL] = 0.1 % on St (c))
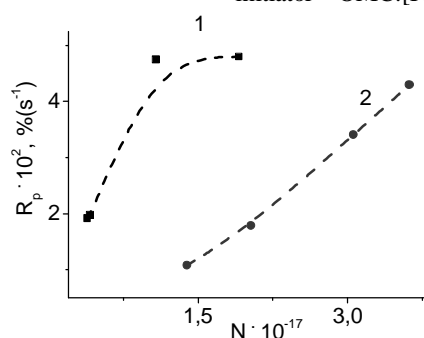

Fig. 16. Dependence of seed copolymerization rate of N-vinyl pyrrolidone and glycidyl methacrylate on the content of "primary" polystyrene nanoparticles (N) with capsulated fluorescein (1) or pyrazoline (2) ([FL] = 0.05–1 %, [PRZ] = 0.01–0.1 % on St

Since SAM is soluble in monomer mixtures and in water, its concentration on the interface of hydrophobic monomers emulsion occurs. As a result, a part of SAM molecules is involved in formation and stabilization of micelles and microdrops of monomer phase dispersed in water, due to formation of adsorbed layer, which ensure stability of micelles, drops and PMP. When the water-soluble FL is capsulated, formation of adsorbed layer of SAM molecules and their participation in copolymerization prevent leakage of phosphor from the nanoparticles core. As it can be seen (Fig. 14), the most of FL initial amount is localized inside of polymer particles, even after their washing. Content of dye in nanoparticles also increase with the growth of their size. It might be explained by formation of tight adsorbed layer of SAM molecules on the particles surface, which prevents release of FL from the microdrops or PMP, as well as their aggregation.

As it is shown in Fig. 14, size of particles and content of phosphor inside are also influenced by the nature of monomer and initial concentration of dye, that determines the topochemistry of polymerization process. Using of OMC that is adsorbed on the surface of drops and obtained nanoparticles leads to initiation of polymerization mainly on the interface and to formation of nanoparticles containing dyes, e.g. water-soluble FL.

Dependence of particles size on monomer conversion (Fig. 15a) confirms high resistance of SAM stabilized dispersions to aggregation. It can be seen that the smallest particles are obtained already at 20 % conversion and further decrease of size is not observed, which is typical of water dispersed polymerization [82]. The reason of this phenomenon is stabilization of PMP and nanoparticles due to formation if functional polymer layer during copolymerization of SAM, localized on the interface. The advantage of developed FL and PRZ capsulation technique consists in the possibility of nanocomposites synthesis with tailored and narrow size distribution (Figs. 15b and 15c) and controlled content of phosphor in their core.

Kinetic curves of grafted polymerization of functional polymer chains to the surface of polystyrene nanoparticles with capsulated phosphors in their core evidence (Fig. 16) that decreasing of the content of initiating primary particles with peroxide moieties localized on their surface in water dispersion causes the deceleration of polymerization rate.

IR-spectra of primary nanoparticles and composite nanoparticles with polystyrene core and grafted shell of poly(NVP-co-GMA) shell contain absorption bands at 1580, 1450 and 720 cm^{-1} corresponding to vibrations of aromatic rings. Absorption bands at 1720 cm^{-1}, attributed to stretching vibrations of C=O groups, in the spectrum of polySt particles are caused by grafting of OMC molecules that contain VA and MA units. Appearance of bands at

1650 and 1460 cm^{-1}, that correspond to stretching vibrations of –N–C=O moiety of NVP and deformation vibrations of –CH$_3$ methacrylate moieties, respectively, evidence grafting of functional polymer shell on the surface of polySt particles. The same is confirmed by the appearance of the set of signals at 1200–1100 cm^{-1} in the spectra of composite particles, corresponding to vibration of epoxide moieties of GMA.

4. Conclusions

Two-stage water dispersed polymerization is a commonly used technique for synthesis of polymer particles with core-shell structure. Application of polymer metal-complex macroinitiators (containing peroxide groups of different reactivity) is a convenient tool for obtaining of the mentioned nanocomposites. On the first stage, formation of monodispersed polymer particles of desired size and functionality is achieved by target variation of concentration of macroinitiator and metal cations in its structure, as well as pH of medium. On the second stage initiation of grafted polymerization from the surface of seeded particles is provided by residual peroxide moieties of macroinitiator. The developed method of monodispersed functional nanocomposites synthesis ensures capsulation substances of different nature, including water soluble phosphors. Unique functional luminescent markers, which were obtained for the first time, can be applied in different devices equipped with filters and designed for registration of fluorescent dyes.

References

[1] Sounderya N., Zhang Y.: Recent Pat. Biomed. Eng., 2008, **1**, 34. https://doi.org/10.2174/1874764710801010034.
[2] Bawa P., Pillay V., Choonara Y., du Toit L.: Biomed. Mater., 2009, **4**, 022001. https://doi.org/10.1088/1748-6041/4/2/022001.
[3] Shunichi K., Niichiro H., Toshihide S. *et al.*: Pat. US 4173696, Publ. Nov. 06, 1979.
[4] Ivanchov S.: Peroxidsoderzhashchiye Iniciatory Emulsionnoy Polymerizacii Vinilnyh Monomerov [in:] Emanuel N. (Ed.) Khimiya Organicheskikh Peroxidov. VPI, Volgograd 1982, 115-136.
[5] Pavluchenko V., Lesnikova N., Ivanchov S. *et al.*: Vsesoyuzniy Seminar po Khimii Ozona, Tbilisi, 1981, 94.
[6] Ivanchev S., Pavluchenko V., Byrdina N.: J. Polym. Sci. A, 1987, **25**, 47. https://doi.org/10.1002/pola.1987.080250106.
[7] Tauer K., Antonietti M., Rosengarten L., Muller H.: Macromol. Chem. Phys., 1998, **95**, 897. https://doi.org/10.1002/(SICI)1521-3935(19980501)199:5<897::AID-MACP897>3.0.CO;2-X.
[8] Tauer K., Kosmella S.: Polym. Int., 1993, **30**, 253. https://doi.org/10.1002/pi.4990300219.
[9] Dicke H.-R., Heitz W.: Colloid Polym. Sci., 1982, **260**, 3. https://doi.org/10.1007/BF01447669.
[10] Martinek K., Yatsimirski A., Levashov A., Berezin I.: Kinetic Theory and Mechanism of Micellar Effects in Chemical Reactions

[in:] Mittel K. (Ed.) Micellization, Solubilization, and Microemulsions, Springer, New York 1977, 489-508. https://doi.org/10.1007/978-1-4613-4157-4_1.
[11] Ivanchev S., Pavlyuchenko V., Rozhkova D.: Vysokomol. Soed. Ser. A, 1974, **16**, 893.
[12] Messner B., Quis P., Schmitt G. *et al.*: Pat. US 5403883 A.; Publ. Apr. 04, 1995.
[13] Bhattacharya A., Misra B.: Prog. Polym. Sci., 2004, **29**, 767. https://doi.org/10.1016/j.progpolymsci.2004.05.002.
[14] Guyot A., Tauer K.: Adv. Polym. Sci., 1994, **111**, 43. https://doi.org/10.1007/BFb0024126.
[15] Piirma I.: Polymeric Surfactants. Marcel Dekker Inc., New York–Basel 1992.
[16] Voronov S., Varvarenko S.: Peroksydovmisni Macromolekuly na Mezhi Rozdilu Phaz. Naukovi Publikaciyi Nacionalnoho Universitetu "Lvivska Polytechnika", Lviv 2011.
[17] Zaichenko A., Mitina N., Shevchuk O. *et al.*: Macromol. Symp., 2001, **164**, 25. https://doi.org/10.1002/1521-3900(200102)164:1<25::AID-MASY25>3.0.CO;2-V.
[18] Voronov S., Kiselyov Eu., Minko S. *et al.*: J. Polym. Sci. A., 1996, **34**, 2507. https://doi.org/10.1002/(SICI)1099-0518(19960915)34:12<2507::AID-POLA24>3.0.CO;2-B.
[19] Tauer K.: Polymer Nanoparticles with Surface Active Initiators and Polymer Initiators [in:] V. Mittal (Ed.) Advanced Polymer Nanoparticles: Synthesis and Surface Modifications, CRC Press, Boca-Raton 2010, 329-359.
[20] Solomko N., Dron I., Budishevskaya O., Voronov S.: Procedia Chem., 2009, **1**, 1567. https://doi.org/10.1016/j.proche.2009.11.005
[21] Pich A., Richter S., Alder H.-J. *et.al.*: Macromol. Symp., 2001, **164**, 11. https://doi.org/10.1002/1521-3900(200102)164:1<11::AID-MASY11>3.0.CO;2-K.
[22] Adler H.-J.P., Pich A., Henke A. *et al.*: New Core-Shell Dispersions with Reactive Groups [in:] E.Daniels (Ed.) ACS Symposium Series. Washington, DC; American Chemical Society, 2001, 276-292. https://doi.org/10.1021/bk-2002-0801.ch019.
[23] Popadyuk A., Tarnavchyk I., Popadyuk N. *et al.*: React. Funct. Polym., 2013, 73, 1290. https://doi.org/10.1016/j.reactfunctpolym.2013.07.002.
[24] Budishevska O., Dronj I., Voronov A., *et al.*: React. Funct. Polym., 2009, **69**, 785. https://doi.org/10.1016/j.reactfunctpolym.2009.06.006
[25] Cheng C., Shu J., Gong S. *et al.*: New J. Chem., 2010, **34**, 163. https://doi.org/10.1039/B9NJ00307J.
[26] Li G., Mohwald H., Shchukin D.: Chem. Soc. Rev., 2013, **42**, 3628 https://doi.org/10.1039/C3CS35517A.
[27] Okubo M., Katsuta Y., Matsumoto T.: J. Polym. Sci. Polym. Lett., 1980, **18**, 481. https://doi.org/10.1002/pol.1980.130180704
[28] Okubo M.: Macromol. Symp., 1990, **35-36**, 307. https://doi.org/10.1002/masy.19900350119.
[29] Okubo M., Shiozaki M., Tsujihiro M., Tsukuda Y.: Colloid Polym. Sci., 1991, **269**, 222. https://doi.org/10.1007/BF00665495.
[30] He X.-D., Ge X.-W., Wang M.-Z., Zhang Z.-C.: J. Appl. Polym. Sci., 2005, **98**, 860. https://doi.org/10.1002/app.22181
[31] Ramli R., Laftah W., Hashim S.: RSC Adv., 2013, **3**, 15543. https://doi.org/10.1039/C3RA41296B.
[32] Jönsson J.-E., Karlsson O.J., Hassander H., Törnell B.: Eur. Polym. J.,2007, **43**, 1322. https://doi.org/10.1016/j.eurpolymj.2007.01.027.
[33] Chern C.S.: Prog.Polym.Sci., 2006, **31**, 443. https://doi.org/10.1016/j.progpolymsci.2006.02.001
[34] Shim S.-E., Cha Y.-J., Byun J.-M., Choe S.: J. Appl. Polym. Sci., 1999, **71**, 2259. https://doi.org/10.1002/(SICI)1097-4628(19990328)71:13<2259::AID-APP17>3.0.CO;2-5.

[35] Gan D., Lyon L.: J. Am. Chem. Soc., 2001, **123**, 7511. https://doi.org/10.1021/ja010609f.

[36] Li W.-H., Stöver H.D.H.: Macromolecules, 2000, **33**, 4354. https://doi.org/10.1021/ma9920691.

[37] Chainey M., Hearn J., Wilkinson M.: Brit. Polym. J., 1981, **13**, 132. https://doi.org/10.1002/pi.4980130310.

[38] Coen E., Lyons R., Gilbert R.: Macromolecules, 1996, **29**, 5128. https://doi.org/10.1021/ma9600567.

[39] Huang Z., Wang C., Li Y., Wang Z.: Colloid Polym. Sci., 2012, **290**, 979. https://doi.org/10.1007/s00396-012-2663-5.

[40] Vanderhoff J., El Aasser M., Micale F. *et al.*: J. Disp. Sci. Tech., 1984, **5**, 231. https://doi.org/10.1080/01932698408943220.

[41] Vanderhoff J., Micale F., El Aasser M., Tseng C.M.: Pat. US 5106903, Publ. Apr. 21, 1992.

[42] Jeong Y.-S., Lee K-W., Ha H.-C.: Pat. US 20050176894, Publ. Aug. 11, 2005.

[43] Adelnia H., Gavgani J.N., Soheilmoghaddam M.: Colloid Polym. Sci., 2015, **293**, 2445. https://doi.org/10.1007/s00396-015-3675-8.

[44] Chu H., Wang H., Ni Z. *et al.*: Particuology, 2008, **6**, 369. https://doi.org/10.1016/j.partic.2008.06.002.

[45] Liao X., Cheng J.; Li L. *et al.*: Polym. Polym. Compos., 2009, **17**, 109.

[46] Huang B., Bai F., Yang X.-l., Huang W.-Q.: Chin. J. Polym. Sci., 2010, **28**, 277. https://doi.org/10.1007/s10118-010-9089-7.

[47] Okubo M., Nakagawa T.: Colloid Polym. Sci., 1992, **270**, 853. https://doi.org/10.1007 / BF00657729.

[48] Okubo M., Shiozaki M.: Polym. Int., 1993, **30**, 469. https://doi.org/10.1002/pi.4990300409.

[49] Minami H., Wang Z., Yamashita T., Okubo M.: Colloid Polym. Sci., 2003, **281**, 246. https://doi.org/10.1007/s00396-002-0766-0.

[50] Lu X., Xin Z.: Colloid Polym. Sci., 2006, **284**, 1062. https://doi.org/10.1007/s00396-006-1482-y.

[51] Sayer C., de Araujo P.H.: Synthesiz of Polymer Particles with Core-Shell Morphologies [in:] V. Mittal (Ed.) Advanced Polymer Nanoparticles: Synthesis and Surface Modifications, CRC Press, Boca-Raton, 2010, 26-60.

[52] Fujibayashi T., Okubo M.: Langmuir, 2007, **23**, 7958. https://doi.org/10.1021/la7007842.

[53] Voronov S., Tokarev V., Datsyuk V., Kozar M.: The 37th General Meeting of the German Colloid Society, German, Dresden 1996, 189. https://doi.org/10.1007/BFb0114468.

[54] Tokarev V., Voronov S., Adler H.-J., *et al.*: Macromol. Symp., 2002 ,**187**, 155. https://doi.org/10.1002/1521-3900(200209)187:1<155::AID-MASY155>3.0.CO;2-H.

[55] Voronov S., Tokarev V., Datsyuk V., *et al.*: J. Appl. Polym. Sci., 2000, **76**, 1228. https://doi.org/10.1002/(SICI)1097-4628(20000523)76:8<1228::AID-APP3>3.0.CO;2-8.

[56] Shevchuk O., Tokarev V., Bukartyk N., Voronov S.: Macromol. Symp., 2007, **254**, 260. https://doi.org/10.1002/masy.200750839.

[57] Kagawa Y., Minami H., Okubo M., Zhou J.: Polymer, 2005, **46**, 1045. https://doi.org/10.1016/j.polymer.2004.11.040.

[58] Kitayama Y., Kagawa Y., Minami H.,.Okubo M.: Langmuir, 2010, **26**, 7029. https://doi.org/10.1021/la904296h.

[59] Jhaveri S., Koylu D., Maschke D., Carter K.: J. Polym. Sci. Part A., 2007, **45**, 1575. https://dx.doi.org/10.1002/pola.21977.

[60] Tang D., Yuan R., Chai Y., An H.: Adv. Funct. Mater., 2007, **17**, 976. https://doi.org/10.1002/adfm.200600462.

[61] Gai L., Li Z., Hou Y.*et al.:* J. Phys. D: Appl. Phys., 2010, **43(44)**, 445001. https://doi.org/10.1088/0022-3727/43/44/445001.

[62] Wang H., Zhang Y., Yan B. *et al.*: Clin. Chem., 2006, **52**, 2065. https://doi.org/10.1373/clinchem.2006.071555.

[63] Shtykov S., Rusanova T.: Russ. J. Gen. Chem., 2008, **78**, 2521. https://doi.org/10.1134/S1070363208120323.

[64] Aslan K., Wu M., Lakowicz J., Geddes C.: J. Am. Chem. Soc., 2007, **129**, 1524. https://doi.org/10.1021/ja0680820.

[65] Shao M., Ning F., Zhao J. *et al.*: J. Am. Chem. Soc., 2012, **134**, 1071. https://doi.org/10.1021/ja2086323.

[66] Liu X., Knauer M., Ivleva N. *et al.*: Anal. Chem., 2010, **82**, 441. https://doi.org/10.1021/ac902573p.

[67] Vaculik P.: Khimiya Monomerov. Inostrannaya literatura, Moskva 1960.

[68] Moldavsky B.; Kernos Y.: Maleyinovyi Anhidrid i Maleyinovaya Kislota. Khimiya, Leningrad 1976.

[69] Hevus O., Kohut A., Fleychuk R. et. al.: Macromol. Symp., 2007, 117. https://doi.org/10.1002/masy.200750818.

[70] Vylenskaya M., Karamov D., Sorokin E. *et al.*: Khimicheskaya Promyslennost ,1979, **7**, 15.

[71] Abramson A.: Povercnosno-Activnye Soyedineniya. Svoystva i Priminenia, Khimia, Leningrad 1981.

[72] Zaichenko A., Mitina N., Kovbuz M. *et al.:* J. Polym. Sci. A., 2000, **38**, 516. https://doi.org/10.1002/(SICI)1099-0518(20000201)38:3<516::AID-POLA18>3.0.CO;2-R.

[73] Zaichenko A., Voronov S., Shevchuk O. *et al.*: J. Appl. Polym. Sci., 1998, **67**, 1061. https://doi.org/10.1002/(SICI)1097-4628(19980207)67:6<1061::AID-APP13>3.0.CO;2-3.

[74] Cherpak V., Stakhira P., Khomyak S. *et al.:* Opt. Mater., 2011, **33**, 1727. https://doi.org/10.1016/j.optmat.2011.05.034.

[75] Bagdasarian Kh.: Theory of Free Radical Polymerization, Israel Program for Scientific Translations, Jerusalem 1968.

[76] Gladyshev G., Popov V.: Radialnaya Polimerizaciya pri Hlubokikh Stadiyah Prevrashcheniya. Nauka, Moskva 1974.

[77] Toroptseva A., Belogorodskaya K., Bondarenko V.: Laboratorniy Praktikum po Khimii i Technolohii Vysokomoleculyarnykh Soyedineniy. Khimiya, Leningrad 1972 .

[78] Neiman R. (Ed.): Prakticheskie Raboty po Koloidnoi Khimii. Coloidnaya Khimia Lateksov i Poverhnosno-Activnykh Soedineniy. Vyshaia shkola, Moskva 1972.

[79] Zaichenko A., Mitina N., Kovbuz M. *et al.*: Macromol. Symp., 2001, **164**, 47. https//doi.org/10.1002/1521-3900(200102)164:1<47::AID-MASY47>3.0.CO;2-F.

[80] Kohut A, Hevus O., Voronov S.: J. Appl. Pol. Sci., 2004, **93**, 310. https//doi.org/10.1002/app.20456.

[81] Smith B.: Infrared Spectral Interpretation: A Systematic Approach, CRC Press, Boca-Raton 1999.

[82] Eliseeva V.: Polimernye Dispersii, Khimia, Moskva 1980.

ЦІЛЬОВИЙ СИНТЕЗ ФУНКЦІОНАЛЬНИХ БІОСУМІСНИХ НАНОКОМПОЗИТІВ БУДОВИ «ЯДРО-ОБОЛОНКА»

Анотація. *Металокомплексні макроініціатори були успішно застосовані для синтезу полімерних нанокомпозитів зі структурою "ядро-оболонка" методом двоступінчатої вододисперсійної полімеризації. На першому етапі формування монодисперсних полімерних частинок бажаного розміру і функціональності досягається внаслідок цілеспрямованої зміни концентрації макроініціатору, вмісту катіонів металів в його структурі, і pH середовища. Ініціювання прищеплювальної полімеризації з поверхні затравкових частинок забезпечується залишковими пероксидними фрагментами макроініціатору.*

Ключові слова: *дисперсійна полімеризація, макроіні-ціатори, композиційні полімерні частинки.*