

N. E. Mitina<sup>1</sup>, V. V. Vistovskiy<sup>2</sup>, A. S. Voloshynovskiy<sup>2</sup>, O. S. Miagkota<sup>1</sup>, A. S. Zaichenko<sup>1</sup>

<sup>1</sup> Lviv Polytechnic National University,

<sup>2</sup> Ivan Franko National University of Lviv

## SCINTILLATION POLYMERIC NANOLAYERS BASED ON BAF<sub>2</sub>

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Method of obtaining scintillation polymer films, loaded with nanoparticles as a result of their nucleation in functional polymer brushes, immobilized on solid substrates was developed. Dependence of size and size distribution of mineral particles formed by nucleation in polymer "brushes" on density of polymer chains packing on substrate, as well as nature and content of oligoperoxide macroinitiators immobilized on the surface, was investigated. Dependence of nanoparticles size on content of carboxyl groups in molecules of surface-active copolymers used as templates was investigated. Polystyrene and poly(styrene-co-acrylonitrile) polymer films, loaded with nanoparticles of fluorides of alkaline earth elements, were characterized with attractive physical and mechanical properties and optical transparency.

**Key words:** Polymer "brushes", template synthesis, scintillation coating, nanoparticles of fluorides of alkaline earth elements, peroxide-containing oligomer surfactants, polymer-mineral nanocomposites.

Мітіна Н. Е., Висоцький В. В., Волошиновський А. С., Мягкова О. С., Заїченко А. С.

## СЦИНТИЛЯЦІЙНІ ПОЛІМЕРНІ НАНОШАРИ НА ОСНОВІ BAF<sub>2</sub>

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Розроблено метод отримання сцинтиляційних полімерних плівок, наповнених наночастинами в результаті їх нуклеації в функціональних полімерних щітках на підкладках. Встановлена залежність розміру та розподілу за розміром частинок, які утворюються, від щільності пакування полімерних ланцюгів на підкладці, а також від природи та вмісту олігопероксидного макроініціатора, іммобілізованого на поверхні. Встановлено залежність розміру наночастинок, отримуваних темплатним синтезом, від вмісту карбоксильних груп в молекулах поверхнево-активних кополімерів – темплатів. Полімерні плівки на основі полістиролу та полі(стирол-ко-акрилонітрил), наповнені наночастинами фторидів лужноземельних елементів, характеризуються високими фізико-механічними показниками та оптичною прозорістю.

**Ключові слова:** полімерні "щітки", темплатний синтез, сцинтиляційні покриття, наночастинок фторидів лужноземельних елементів, олігопероксидні поверхнево-активні модифікатори, полімер-мінеральні наноккомпозити.

**Problem statement.** Obtaining of new composite polymer-mineral nano- and micro-sized materials with a set of desired chemical, biological, physical, mechanical and other specialized, like optical, fluorescent, scintillation properties resulted in rapid progress of advanced technologies. Appearance of these nanocomposites provided development of new methods for express medical diagnostics, registration of X-ray and neutron radiation, etc. Formation of thin-layer X-ray, neutron, and ionizing radiation detectors is prospective field of applying transparent scintillation and luminescent polymer composites. One of existing approaches of transparent polymer-mineral composites synthesis consists on formation of nanolayer of scintillation particles immobilized in polymer brushes.

**Analysis of last investigations and publications.** Some methods of obtaining thin-layered detectors were described in literature. For example, neutron radiation detectors were synthesized by polymerization method in the presence of mineral particles. Thin capillaries were served as hard templates that provided obtaining plastic scintillators shaped as rods with diameter 200 microns. Also, it is known method of forming radiation detectors using large amount of relatively thin polymer layers based on polyvinyl toluene

[1]. Other attractive materials for technological processes are X-ray image detectors [2]. In modern devices to convert of X-ray radiation into visible light scintillation panels are applied. For this aim, utilizing of thick phosphor layers is unacceptable, because of increasing of light scattering, resulting in deterioration of image resolution. Scintillation panels can be obtained by sublimation of nanocrystals rods of CsI, for example, on substrate. To protect scintillation layer of nanocrystals, it is covered with optically transparent polymers, like copolymers of vinyl acetate and butyl acrylate, styrene, acrylonitrile and butadiene, etc. The transmittance of polymeric layer must be at least 70 %. The drawback of such "panel" scintillators is that formation of a crystals layer is conducted on hard substrates. Monolayers or arrays of arranged mineral particles located in polymer films gained an interest of researchers due to prospects of theirs application in optics, electronics and for designing different sensors. However, formation of arranged nanoparticle layers (nearly two-dimentional) in polymer matrix require some special techniques, and it can not be achieved with direct introduction of particles in polymer by casting, spin-coating or dip-coating methods. Freely suspended gold nanoparticle arrays were fabricated by encapsulation into layer-by-layer nanomembranes [3]. Related method of formation nanoparticle layers was described in paper [4] and consists with three consecutive stages. In the first step silver nanoparticles were self-assembled in monolayer on poly(vinylpyridine) film. The next steps involved coating the nanoparticles surface with dimethylsiloxane prepolymer and curing this coating, the obtained film was removed from the substrate. Such methods are quite simple and reliable, but they don't provide formation of long range ordered nanoparticle layers. Block-copolymer lithography is another promising approach of loading polymers with mineral well-arranged layers of nanoparticles, based on applying thin films of block-copolymers on substrates [5]. Due to the limited compatibility of components in such systems, theirs microphase distribution is observed, which in some cases leads to formation of self-assembled structures that in first approximation can be represented as domains of one block, distributed in a matrix of another [6]. The size, shape and orientation of the domains can be controlled by varying the relative and absolute length of polymer blocks, the nature of the substrate, conditions of formation and height of film, and other parametrs [6]. In this way large amount of two- and three-dimensional structures can be obtained and used later as templates for synthesis well-arranged nanoparticled arrays using mechanism of theirs selective adsorption [7]. In [8] was reported about formation of silver nanolayers in polymer brushes, that served as soft templates. To create polymer template, thin film of a polymer containing reactive groups was deposited onto the substrate surface. Then, it was covered layer-by-layer with polystyrene and polydymethylsilocsan film (stamp) employing capillary force lithography (CFL). The complete assembly was annealed at 120°C. Selective melting of polystyrene film under stamp resulted in patterning formation with alternating fragments of polystyrene and reactive epoxy-containing polymer. Layer of poly(vinylpyrrolidone) that interact with epoxy groups was attached to the surface of template. Immobilization of Ag nanoparticles in polymer brushes was accomplished thought dip-coating method. Adsorption of metal nanoparticles occurred due to theirs affinity of poly(vinylpyrrolidone) [9]. Then well-arranged Ag nanoparticled layers were transferred to polydymethylsilocsan film with printing method. As a result, transparent polymeric films containing 2D arrays of silver nanoparticles with different polarizing sensitive optical properties were obtained.

**The aim of this paper is** formation of polymer brushes using polyfunctional macroinitiators immobilized on solid substrates; obtain nanolayers of scintillation particles loaded in polymer brushes, study peculiarities of particles nucleation into polymer brushes and possibility of particle size regulation as well as thickness of formed particle layer and homogeneity of theirs distribution on the substrate.

**Experimental. Materials:** *Metal salts:* barium chloride  $\text{BaCl}_2 \times 2\text{H}_2\text{O}$  (Aldrich), potassium fluoride  $\text{KF} \times 2\text{H}_2\text{O}$  (Aldrich). *Monomers:* 2-carboxyethyl acrylate (CEA), poly(ethylene glycol) methacrylate  $M_N \sim 2000$  g/mole (PEGacr) – were commercially available from Sigma-Aldrich and used without additional purification. Peroxide-containing monomer 5-tert-butylperoxy-5-methyl-2-hexene-3-yne (VEP), synthesized according to known technique [10],  $[\text{O}] = 8,7\%$ ,  $d_4^{20} = 867 \text{ kg/m}^3$ . *Solvents:* acetone, dioxane, toluene (Merck) – were used without additional purification. *Scintillation materials:* p-terphenyl (pTP) (Acros), 1,4-bis-(5-phenyloxazole-2)benzene (POPOP) (ABCR) *Polymers for thin scintillation composite films* – polystyrene (PSt) and copolymer of styrene and acrylonitrile (poly(St-co-An), synthesized by

thermal self-initiated block copolymerization.  $\gamma$ -(Aminopropyl)triethoxysilane (APTES)(Aldrich) – used for modification of sital substrates without additional purification.

*Surface – active oligoperoxide macroinitiators (SOM)* with side peroxide groups, synthesized according to known technique [11] via radical polymerization. All prepared polymers were washed and dried to constant mass at room temperature and under a vacuum.

Oligoperoxide metal complexes (OMC) were obtained via complexation of reactive oligoperoxide surfactant – copolymer of vinylacetate, VEP and maleic anhydride – poly(VA-co-VEP-co-MA) and cations  $\text{Cu}^{2+}$  in methanol. Structure and main characteristics of oligoperoxide macroinitiators are shown at Fig. 1 and in Table 1.

Table 1

Characteristics of oligoperoxide macroinitiators

Sample	Composition of monomer mixture, % <sub>mol</sub>				Copolymer composition, % <sub>mol</sub>				[Cu <sup>2+</sup> ], %	Mn, g/mole
	VA	VEP	MA	GMA	VA	VEP	MA	GMA		
oligo(VEP-co-GMA)	-	25.0	-	75.0	-	22.0	-	78.0	-	4000
OMC Cu <sup>2+</sup>	33.3	33.3	33.4	-	22.8	32.2	45.0	-	0.92	2000

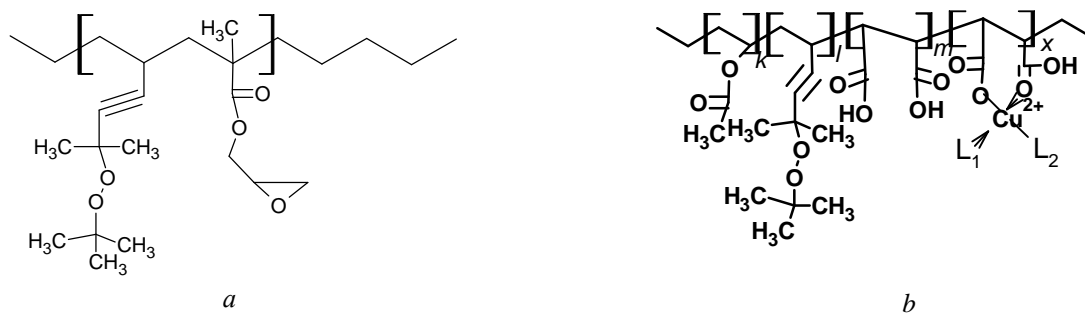


Fig. 1. Structures of oligoperoxide macroinitiators: oligo(VEP-co-GMA) (a) and OMC – metal complex of  $\text{Cu}^{2+}$  with oligo(VA-co-VEP-co-GMA) ligand (b)

**Methods:** Formation of polymer brusher nanolayers on glass substrate was carried out in few steps: 1) modification with amine-containing organosilicon APTES, 2) chemical adsorption of polyfunctional oligoperoxide macroinitiators and 3) grafting hydrophilic polymer chains via radical polymerization to substrate surface. Firstly, sital waffles were treated with 0,1 % solution of APTES in acetone at 323 K for 5 hours, then washed with acetone several times and dried. Next, they were treated in 1 % solution of oligoperoxide in dioxane at 323 K for 5 hours, washed several times with dioxane, acetone and dried. At the third stage, grafted radical copolymerization of CEA and PEGacr monomer mixture to the surface of modified substrate initiated by peroxide groups of immobilized macroinitiator chains was carried out. In typical polymerization procedure substrates were dipped in 100 ml of 1M monomer solution in dioxane for 8 hours at 353 K for oligo(VEP-co-GMA) macroinitiator and 323 K for OMC. Then, they were washed with acetone and dioxane.

Fluoride metal nanoparticles were loaded into polymer brushes as follows: substrates with immobilized polymer brushes were placed in reactor, containing 100 ml of distilled water, for 8 hours at room temperature. Previously prepared 1 % water solution of barium chloride  $\text{BaCl}_2$  was added to reactor and left for 5 hours at room temperature. Next, solution of KF was added dropwise in three-time excess relatively to  $\text{BaCl}_2$ . As a result, white precipitate of  $\text{BaF}_2$  was obtained. After the grafting was complete, substrates were taken out from reactor, washed multiply with distilled water and dried.

Thin polymer films for scintillation composites were prepared from 35 % solution of PSt or poly(St-co-An) in toluene containing fluorescent substances – pTP and POPOP (1,5 % and 0,02 % by polymer weight). Layer of viscous polymer solution 5 mm height was deposited onto the surface of substrate. Films

of 0,5 mm were formed after solvent vaporation treatment at 333 K for 3 hours. Then, polymer films were removed from the substrate.

**Analysis:** Visualization of grafted polymer brushes, as well as obtained in these brushes nanoparicles, was performed by atom force microscopy at AFM XE120 (ParkSystemsCorp). Deformation or any other undesired changes in the structure of surface layer were avoided since semicontact mode of AFM was used and the pressure on surface was minimal. Similar images that were got over different time periods of scanning, evidenced about reproducibility of results. Imaged were processed with XEI1.8.0 Build16 (ver 2011/02/21) (ParkSystemsCorp). Content of the mineral residue in polymer films was determined by elemental analysis. Physical and mechanical properties of polymer films were determined by standard techniques such as hardness by pencil test (Wolff-Vilborn method), adhesion (method of net cuts) and elasticity of films evaluation (mandrel bend test of attached organic coatings). Luminescent spectra were registered by automatic installation. To excite luminescent hydrogen lamp as excitation source ( $\lambda=260$  nm) with monochromator MDR-2 were used. Samples were placed in transparent quartz cuvette. Luminescent signal was intensified by photomultiplier FEU-100 and recorded with computer software.

**Discussion.** *Formation of scintillation nanolayer in polymer brushes.* To produce thin-layer scintillation films we used a technique of monolayers formation deposited on surface of substrates utilizing scintillation particles. Procedure of monolayers fabricating is illustrated in Fig. 2. In contrast to known approaches described in the literature where monolayers of mineral nanoparticles introduced into polymer brushes are obtained due to theirs selective adsorption from dispersion [12], in our case, formation of nanoparticles in grafted to substrate polymer functional brushes is occurred as a result of nucleation process. Size and polydispersity of obtained mineral particles are determined by type, microstructure, content and density of polymer brushes.

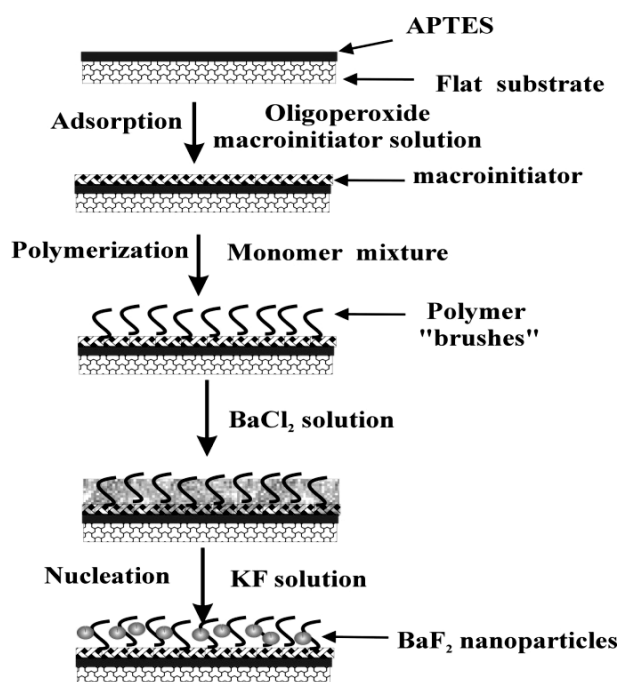


Fig. 2. Scheme of nanoparticles layers formation in functional polymer brushes

Chemical adsorption of oligoperoxide initiators to the surface of amine-modified substrate is provided by epoxy and carboxyl groups in oligoperoxide chains. AFM images analysis gives the quantitative results concerning height of adsorbed layers of different macroinitiators depending on their initial solution concentrations (Fig. 3).

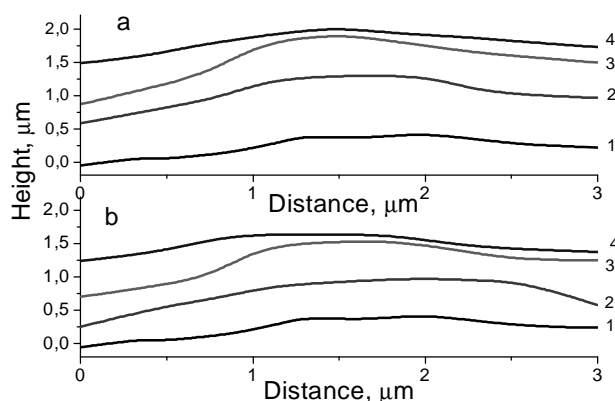


Fig. 3. Height profiles (calculated from topographic AFM) of adsorbed layers of APTES (1), oligoperoxide macroinitiators – oligo(VEP-co-GMA) (a) and OMC (b), obtained from their initial solutions with different concentration: 2 – 0,5 %, 3 – 1,0 %, 4 – 3 %

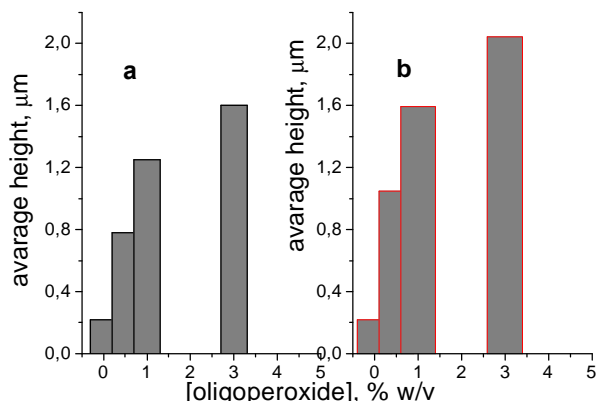


Fig. 4. Dependence of adsorbed layers height formed by oligo(VEP-co-GMA) (a) and OMC (b) on their concentration in solutions

Growth of oligoperoxide concentration in solution leads to increasing of height of its adsorbed layer. Moreover, adsorption of OMC results in producing higher layers that explains, as we suggest, with efficient interaction of carboxyl groups, containing in its structure, and amino groups of APTES resulting in obtaining stable complexes of salt type [13] on the surface of substrate (Fig. 4).

Peroxide containing moieties of functional macroinitiators adsorbed on substrates enable grafting to radical polymerization and formation films of polymer brushes. AFM images of substrates before and after grafting polymerization illustrated in Fig. 5 demonstrate considerable changes of profile and morphology of substrate surface caused by grafting polymer chains.

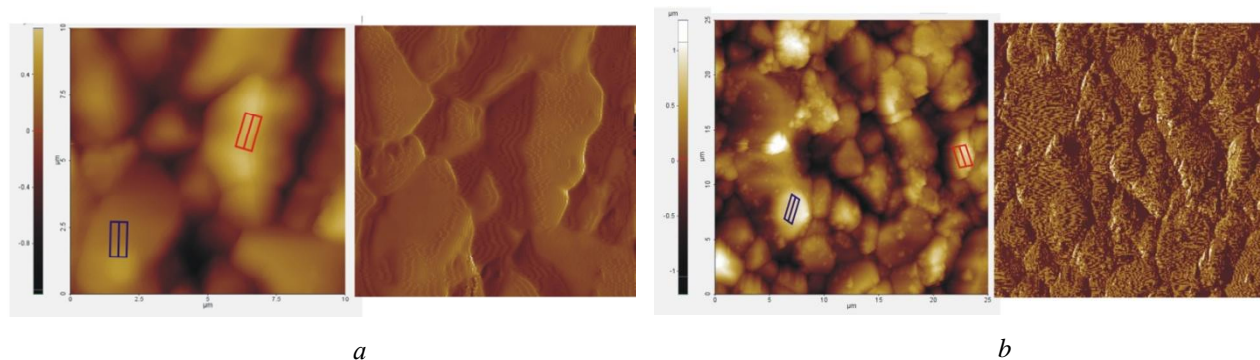


Fig. 5. AFM images of substrate with adsorbed macroinitiator OMC (a) and grafted polymer brushes of CEA and PEGac (b) (topographic and contrast image)

Peroxide bonds of immobilized on substrates macroinitiators decompose with formation of free radicals at wide temperature range due to different mechanisms. Polymerization can be initiated starting at 80 °C by oligo(VEP-co-GMA) and 25 °C by OMC. Decomposition of VEP units of oligo(VEP-co-GMA) occurs by homolytic dissociation with formation of two radicals [14]. In case of oligoperoxide metal complex OMC, homolysis and single electron transfer take place simultaneously when VEP units decompose. As a result macroradicals mainly are formed that enhance grafting copolymer chains to substrate [15].

Decreasing temperatures of polymerization results in grafting of longer polymer chains that is confirmed by increasing of height of obtained films and density of polymer brushes, when OMC is used to initiate polymerization (Fig. 6).

Nucleation of metal fluorides from correspond solutions leads to embedding of nanoparticle monolayers into polymer matrix, immobilized in substrates. Size and shape of obtained nanoparticles can be regulated by nature of salts, functionality and content (density) of polymer brushes.

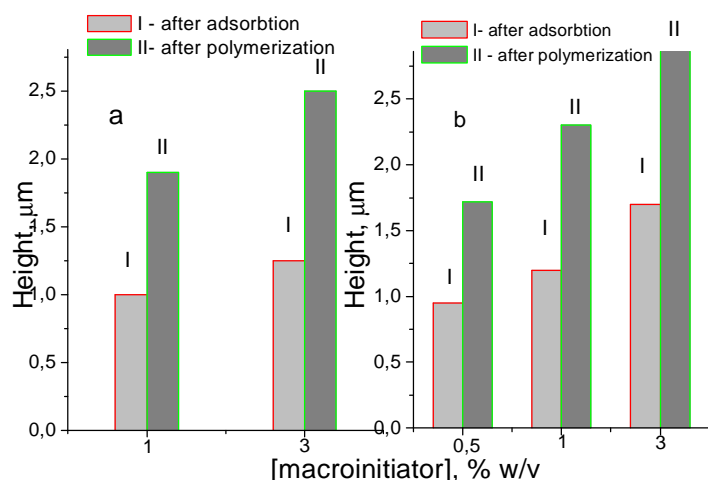


Fig. 6. Height of immobilized on substrate films obtained before (I) and after (II) grafted polymerization of CEA and PEGacr monomer mixture, initiated by oligo(VEP-co-GMA) (a) and OMC (b) at their different initial concentration in solution before adsorption

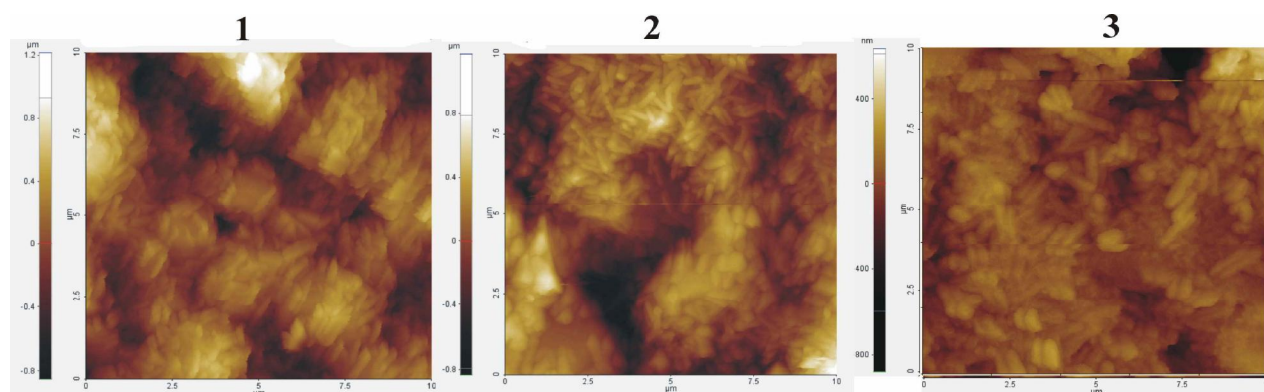


Fig. 7. AFM images of BaF<sub>2</sub> particles localized in poly(CEA-co-PEGacr) chains, grafted to substrate: 1 – height of polymer brushes – 1,9 μm (initiator – oligo(VEP-co-GMA), [initiator]=1 % w/v), 2 – height of polymer brushes – 3,0 μm (initiator – OMC, [initiator]=3 % w/v), 3 – height of polymer brushes – 1,7 μm (initiator – OMC, [initiator]=0,5 % w/v))

AFM images of BaF<sub>2</sub> particles layer, obtained in polymer films with different density of grafted polymer chains are illustrated in Fig. 7. Synthesized particles, as demonstrate the images, are ellipse shaped. To characterize the size, length and height of particles, as well as theirs nucleated number per square unit, were determined. Results are shown in Table 2.

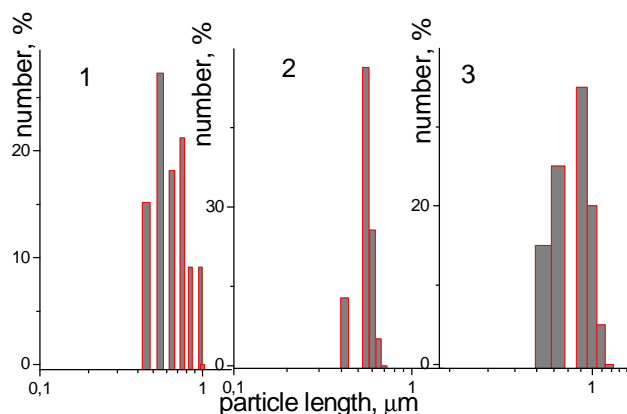


Fig. 8 Size distribution of BaF<sub>2</sub> particles, obtained in poly(CEA-co-PEGacr) brushes with different density: 1 – height of polymer brushes – 1,9 μm (initiator – oligo(VEP-co-GMA), [initiator]=1 % w/v), 2 – height of polymer brushes – 3,0 μm (initiator – OMC, [initiator]=3 % w/v), 3 – height of polymer brushes – 1,7 μm (initiator – OMC, [initiator]=0,5 % w/v))

Relatively big particles with height polydispersity are formed in the surface of substrate with lower density of grafted polymer chains (Fig. 7, image 1 and 3 – height of films 1,9 and 1,7  $\mu\text{m}$  respectively), unlike when film with more tightly packed polymer brushes (height of polymer brushes – 3,0  $\mu\text{m}$ ) is used (Fig. 8).

It is also evident from Fig. 8 that type of macroinitiator doesn't affect on size of obtained particles, but only on the density of grafted polymer brushes to the surface of substrate that on its turn determines parameters of nanoparticles, which are formed through nucleation process (Table 2).

Polymer scintillators based on layers of fluorescent nanoparticles incorporated into flexible transparent polymer films are prospective novel materials that can be applied for needs of such fields like optics, electronics or for construction sensors for registration X-ray and neutron irradiation.

Table 2

Characteristic of  $\text{BaF}_2$  particles obtained in poly(CEA-co-PEGacr) brushes

Characteristic of polymer film		Particle size (average)		Standart deviation of particle size		Number of particles per $10 \mu\text{m}^2$
Macroinitiator	Height of film, $\mu\text{m}$	Lenght ( $l$ ), $\mu\text{m}$	Height ( $h$ ), $\mu\text{m}$	$Dl$ , $\mu\text{m}$	$Dh$ , $\mu\text{m}$	
oligo(VEP-co-GMA) (1 %)	0,19	0,66	0,22	0,15	0,07	52
OMC (3 %)	0,30	0,52	0,14	0,06	0,03	83
OMC (1 %)	0,24	0,51	0,15	0,08	0,05	70
OMC (0,5 %)	0,17	0,78	0,23	0,11	0,06	60

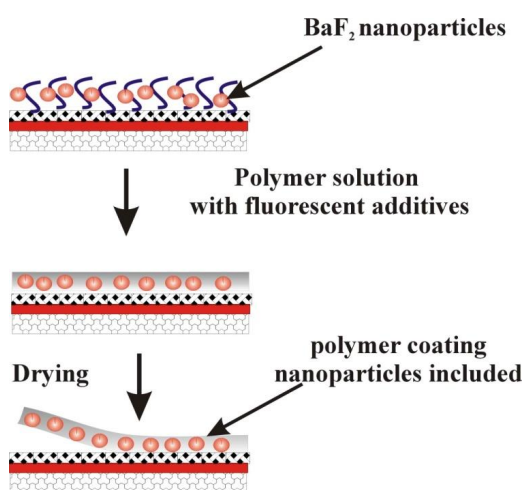


Fig. 9. Scheme of thin coating fabrication based on incorporated nanoparticles, obtained by their nucleation in polymer brushes

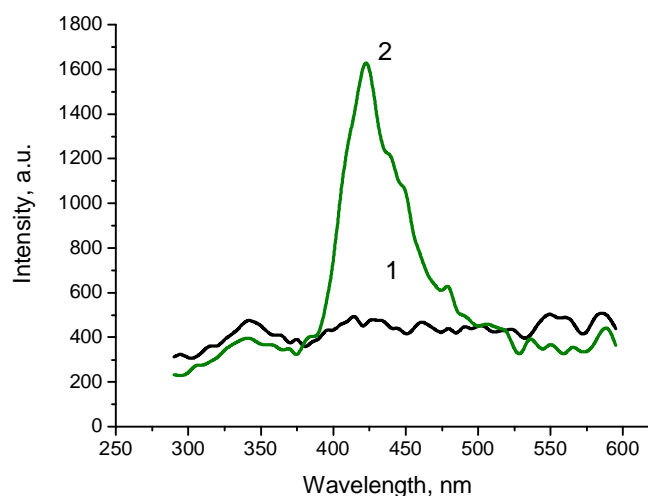


Fig. 10. Luminescent intensity spectra of scintillation PS-An (1) films with loaded organic phosphors and doubled layered PSTt-An scintillation composites ( $h=0,15 \text{ mm}$ ) based on  $\text{BaF}_2$  nanoparticles loaded into polymer brushes grafted to substrate (2)

**Formation of scintillation film.** Scintillation polymer “sandwich” coating were fabricated by applying film of optically transparent polymer (PSt or poly(St-co-An)) onto the surface of mineral nanoparticle layer loaded in polymer brushes. As a result, layer of nanoparticles is incorporated in polymer coating using printing (pattern) method (Fig. 9).

Luminescent properties of thin scintillation films are demonstrated on corresponding spectra (Fig. 10). Emission intensity of films filled with  $\text{BaF}_2$  nanoparticles is four times higher relatively to unfilled ones.

After all procedures are completed, transparent, elastic and firm film with intense luminescence and scintillation properties is fabricated (Table 3, Fig. 10).



Table 3

Characteristic of thin polymer films, filled with BaF<sub>2</sub> nanoparticles

	Height of film, mm	Content of nanoparticles in film, % w/w ( <i>mineral residue</i> )	Pencil test (Wolff-Vilborn method)	Elasticity of films (mandrel bend test), Ø, mm	Transmittance, %	Luminescent intensity, relatively to h=0,3 mm
PSt solution with 0,2 % pTP and 0,02 % POPOP	0,1	1,38	>2H	10 mm	73	1,69
Poly(St-coAn) solution with 0,2 % pTP and 0,04 % POPOP	0,1	1,43	>2H	5 mm	78	1,38

**Conclusions.** Novel technique of scintillation films preparation is proposed, according to which nanoparticle layer is loaded into grafted to substrate polymer brushes due to nucleation process. Size and size distribution of mineral particles dependence on density of polymer brushes grafted to substrate, structure and quantity of absorbed oligoperoxide macroinitiator is studied.

1. Pat. 7372041 United States. Neutron detectors and related methods/ Vivek Nagarkar; [etal.]; Assignee: Radiation Monitoring Devices, Inc. – Publ.: May 13, 2008// 11/624010. 2. Pat. 6563120 United States. Flexible irradiation detectors scintillator / Charles E. Baldwin; [et al.]; Assignee: Ronan Engineering Co. – Publ.: May 13, 2003// 10/091970. 3. Freely Suspended Gold Nanoparticle Arrays/ C. Y. Jiang, S. Markutsya, H. Shulha, V. V. Tsukruk. // *Adv. Mater.* – 2005. – Vol. 17. – P. 1669–1673. 4. Fabrication of Two-Dimensional Assemblies of Ag Nanoparticles and Nanocavities in Poly(dimethylsiloxane) Resin / S. Malynych, H. Robuck, G. Chumanov // *Nano Lett.* – 2001. – Vol. 1. – P. 647–649. 5. Hamley I. W. Nanostructure fabrication using block copolymers/ I. W. Hamley // *Nanotechnology.* – 2003. – Vol. 14 – R39–R54. 6. S. Förster. From self-organizing polymers to nano- and biomaterials / S. Förster, M. Konrada // *J. Mater. Chem.* – 2003. – Iss. 13. – P. 2671–2688. 7. Терехин В.В. Формирование упорядоченных ансамблей наночастиц методами блоксополимерной литографии / В. В. Терехин, О. В. Дементьева, В. М. Рудой // *Успехи химии.* – 2011. – Т. 80 (5). – С. 477–497. 8. B. Zdyrko. Fabrication of optically active flexible polymer films with embedded chain-like arrays of silver nanoparticles / B. Zdyrko, M. K. Kinnan, G. Chumanov, I. Luzinov // *Chem. Commun.* – 2008. – Iss. 11. – P. 1284–1286. 9. Malynych S. Poly(Vinyl Pyridine) as a Universal Surface Modifier for Immobilization of Nanoparticles/ S. Malynych, I. Luzinov, G. Chumanov // *J. Phys. Chem. B.* – 2002. – 106. – P. 1280. 10. Юрженко Т. И. и др. Синтез и исследование ненасыщенных полимеризующихся гидроперекисей // *Успехи химии органических перекисных соединений и аутоокисление.* – М.: Химия, 1969. – С. 59–64. 11. Kinetic features and molecular weight characteristics of terpolymerization products of the systems based on vinyl acetate and 5-tert-butyl-peroxy-5-methyl -1-hexene-3-yne / A. S. Zaichenko, S. A. Voronov, O. M. Shevchuk [etal.] // *Journal of Applied Polymer Science.* – 1997. – Vol. 67. – P. 1061–1066. 12. Matthew G. Moffitt. Self-Assembly of Polymer Brush-Functionalized Inorganic Nanoparticles: From Hairy Balls to Smart Molecular Mimics // *J. Phys. Chem. Lett.* – 2013. – Vol. 4 (21). – P. 3654–3666. 13. Донцов А. А. Процессы структурирования эластомеров – М.: Химия, 1978. – 288 с. 14. Voronov S. Heterofunctional polyperoxides. Theoretical basis of their synthesis and application in compounds/ Voronov S., Tokarev V., Petrovska G. – Lviv: State University "Livivska polytechnica", 1994. – 84 p. 15. A. Zaichenko, N. Mitina, M. Kovbuz, I. Artym, S. Voronov. Low-temperature surface-active complex-radical oligo (di-tert.alkyl) peroxide initiators and curing agents // *Macromol. Symp. (React. Pol.).* – 2001. – No. 164. – P. 47–71.