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Polymer composite based on polystyrene containing GdF_3 nanoparticles

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Polymeric polystyrene-based composites containing GdF_3 nanoparticles stabilized by ammonium dihexadecyldithioposhate and β-styrylphosphonic acid were obtained by radical bulk polymerization. Use of a component β-styrylphosphonic acid, capable of copolymerizing with styrene, as a modifier of GdF_3 surface allows to increase substantially the content of GdF_3 nanoparticles in polystyrene plastic scintillator without changing its scintillations properties.

Методом радикальной полимеризации стирола в блоке получены полимерные композиты, содержащие наночастицы фторида гадолиния, стабилизированные дигексадецилдитиофосфатом аммония и β-стирилфосфоновой кислотой. Модификация поверхности наночастиц β-стирилфосфоновой кислотой, способной к сополимеризации со стиролом, позволяет существенно повысить содержание наночастиц в полистирольном пластмассовом сцинтилляторе с сохранением его сцинтилляционных свойств.

1.Introduction

Organic scintillators with gadolinium additives are widely used for various physical tasks, related to neutron or neutrino registration. A special place among them is occupied by plastic scintillators, because they can be of virtually unlimited size, and can have a relatively high scintillations efficiency, low response time and possibility of composition modification. Plastic scintillators with a several percent's level of gadolinium ions content from general mass of polymer are necessary for many experiments in high energy physics, especially for neutrino registration.

However, inserting large concentrations of gadolinium compounds in a polymer, as a rule, leads to considerable loss of a scintillator light yield. As gadolinium additives most researchers use compounds well soluble in an initial monomer: gadolinium acetylacetonate [1], $Gd(NO_3)_3$·TBP complex [2, 3], complex of gadolinium compounds with hexametyltriamide of phosphoric acid [4, 5], gadolinium isopropylate [6] and carboxylates [7, 8]. But plastic scintillators obtained in such a way do not contain sufficient amount of gadolinium, not stable in time and have considerably low light yield comparing to samples without additives.

A number of methods is recently worked out for synthesis of hydrophobic nanoparticles of lanthanide compounds (fluoride, oxides), which are high dispersible in nonpolar organic environments [9–15]. It allows inserting Gd-nanoparticles to a polymeric base of a plastic scintillator by the *in situ* method of polymerization, when nanoparticles are inserted directly in a monomer before polymerization.

So, developing methods of nanoparticles surfaces modification, which provide the maximum dispersion of Gd-nanoparticles in a polystyrene base of a plastic scintillator without disturbing its scintillations properties, is the question of the hour of plastic scintillators technology.

2. Experimental

In our study we used following reagents: 1-hexadecanol (Merck, for syntheses, 95.0 %), phosphorus pentasulphide (Fluka AG, ?98.0 %), dichloromethane (for liquid chromatography, Merck, ≥99.9 %), hexane (Sigma-Aldrich, 95.0 %), methanol (Sigma-Aldrich, 99.8 %), Gd_2O_3 (Sigma-Aldrich, 99.9 %), nitric acid (Ukraine, 59.3 %), sodium fluoride (Ukraine, 99.5 %), styrene monomer (Aldrich, 99.0 %, distillation), phosphorus pentachloride (Sigma-Aldrich, 95.0 %), toluene (Merck, 99.0 %), isopropanol (Aldrich, ≥99.7 %), benzoyl peroxide (recrystallization from methanol/chloroform), triethylamine (Sigma-Aldrich, ≥99.0 %), ammonia solution (Ukraine, 25.0 %).

Gadolinium nitrate $Gd(NO_3)_3 \cdot 6H_2O$ was obtained by dissolving gadolinium oxide in nitric acid with further elimination of nitric acid and solvent. After that, gadolinium nitrate was purified by recrystallization from water and was dried in a vacuum by sodium hydroxide for 2 days.

Ammonium dihexadecyldithiophosphate was synthesized according to the method described in [9]. This P_2S_5 is dissolved in 1-hexadecanol by heating, the suspension was transferred in hexane and ammonia was bubbled through this solution. The resulting precipitate was separated by filtration, washed by hexane, and dried (M.p. 112–115°C).

The GdF_3 nanoparticles were obtained by precipitation in the presence of ammonium in a dihexadecyldithiophosphate methanol/water. The solution of ammonium dihexadecyldithiophosphate and NaF in methanol/water was heated to homogenization. A solution of $Gd(NO_3)_3 \cdot 6H_2O$ in water was added dropwise and then cooled to room temperature. The precipitate was separated by centrifugation and was washed subsequently with water and methanol. The particles were further purified by dispersing in dichloromethane and precipitating by the addition of isopropanol. After separation by centrifugation, the particles were dried on P_2O_5 in a vacuum for 24 h. Obtained GdF_3 nanoparticles, can be dispersed in non polar solvent such as toluene, dichloromethane, and styrene.

β-Styrylphosphonic acid was synthesized according to the method described in [16]. To PCl_5 suspended in benzene the styrene was added under cooling and interfusion. After the crystalline adduct was hydrolyzed with H_2O under cooling. The resulting precipitate was filtered and dried in air (M.p. 140–142°C).

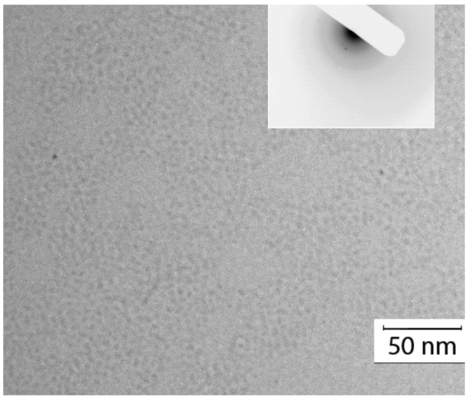

Fig. 1. TEM pictures of GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate.

The GdF_3 nanoparticles modified by β-styrylphosphonic acid were prepared by mixing GdF_3 nanoparticles with ammonium dihexadecyldithiophosphate with β-styrylphosphonic acid and triethylamine in a dichloromethane during twenty-four hours and precipitating them by of isopropanol.

Polymeric compositions were synthesized by radical bulk polymerization a dispersions nanoparticles in styrene using of benzoyl peroxides (0.5 wt. % of the monomer) as the initiator at 80°C during 3th twenty-four hours.

The got matters were studied by means of IR spectroscopy using a SPECTRUM ONE (Perkin Elmer) Fourier IR Spectrophotometer.

Light yield of polystyrene scintillators was measured by a scintillation spectrometer. The spectrometric section of the spectrometer consisted of Hamamatsu R1307 photomultiplier and a charge-digit convertor LeCrou 2249A. Samples excitation was made by 0.975 MeV electrons from a Bi-207 source with a collimator.

The morphology of nanoparticles dusts was studied by means of translucent electron microscope EM-125 (Selmi, Ukraine).

3. Results and discussion

Recently authors of [17] used ammonium dihexadecyldithiophosphate as the surfactant for the polystyrene-platinum compositions obtaining. This allowed to insert up to 8 wt. % of Pt in polystyrene. Therefore to obtain the GdF_3 nanoparticles dispersion in styrene we synthesized GdF_3 nanoparticles with surface modified by ammonium di-

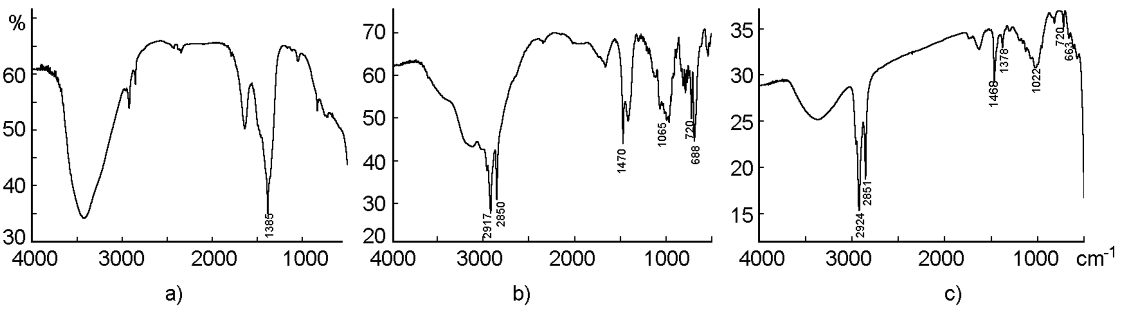

Fig. 2. IR spectra of GdF_3(a), ammonium dihexadecyldithiophosphate (b) and GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate (c).

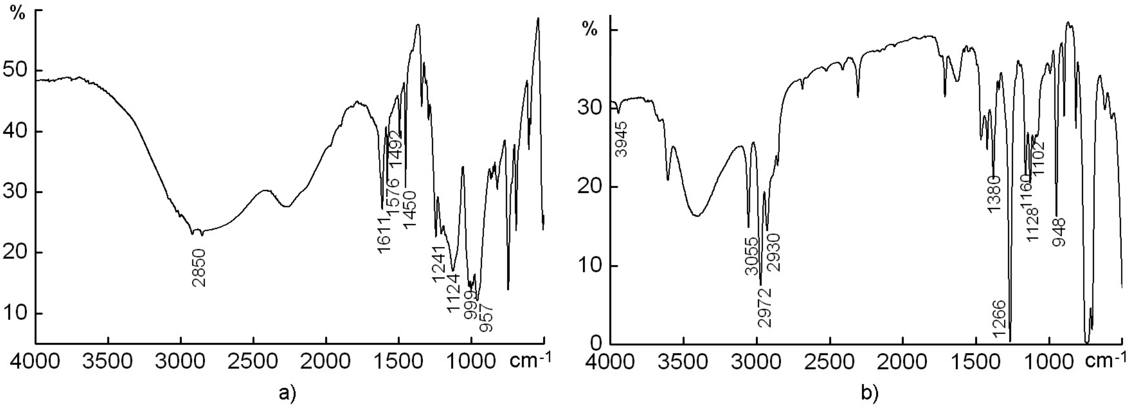

Fig. 3. IR spectra of β-styrylphosphonic acid (a) and GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate (b) and β-styrylphosphonic acid.

hexadecyldithiophosphate according to the method described in [13]. The surface modifier protects the particles at the synthesis stage against aggregation in organic nonpolar solvents, controls the growth and size of the particles.

TEM picture of GdF_3 nanoparticles stabilized ammonium dihexadecyldithiophosphate is shown in Fig. 1. It follows from the figure that nanoparticles, as a rule, have a size of 1–5 nm. IR spectra as ammonium dihexadecyldithiophosphate (Fig. 2) and surface modified GdF_3 nanoparticles with ammonium dihexadecyldithiophosphate (Fig. 3), are characterized by a sequence of intensive bands, which position practically does not depend on the surfactant state. As authors of [18] mention, 1470 cm^{-1} (Fig. 2b) and 1468 cm^{-1} (Fig. 2c) bands correspond to the deformation vibrations of C–H groups. Bands at 2917 cm^{-1} and 2850 cm^{-1} (Fig. 2b), 2924 cm^{-1} and 2851 cm^{-1} (Fig. 2c) correspond to the stretching vibrations of C–H groups and the band of low intensity at 720 cm^{-1} (Fig. 2b,c) — to the pendulum vibrations of ($-CH_2$) group [19].

Bands, characterizing vibrations of (P)–O–C, 1064 cm^{-1} (Fig. 2b) and 1022 cm^{-1} (Fig. 2c), -P=S 688 cm^{-1} (Fig. 2b) and 663 cm^{-1} (Fig. 2c, relative intensity decreases in the adsorbed state), displaced toward low frequency for adsorbed surfactant, that determined, presumably, by influence on IR spectra the co-ordination of dithiophosphate-ion with the ions of gadolinium on the surface of GdF_3 nanoparticles. It should be noted, that 1385 cm^{-1} and 1378 cm^{-1} bands (Fig. 2a and 2c) indicate a presence of several nitrate-ions adsorbed on the surface of GdF_3, which is determined by the synthesis conditions.

Colloidal solution of obtained nanoparticles in styrene with 0.2, 0.5, 1.0 mass. % concentration of nanoparticles in a monomer, was used for further polymerization. It was founded, that after polymerization polymers samples lose their transparency, which indicates the aggregation and even sedimentation of nanoparticles. This aggregating can be reduced by using an additional component able to polymerization, which will provide an aggregation stability of nanoparticles due to formation of cova-

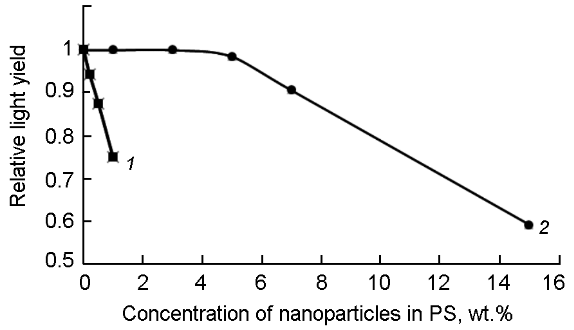

Fig. 4. Relative light yield of Gd-activated scintillators vs. nanoparticles content: *1* — GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate, *2* — GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate and β-styrylphosphonic acid.

lent bonds with the polystyrene molecules and thus fix nanoparticle in the polymer bulk.

As such a component, we used β-styrylphosphonic acid which can be copolymerized with styrene [20]. At the same time, this monomer is not polymerizing along. This allows to use no inhibitors of polymerization during the synthesis of nanoparticles. Moreover, phosphonic acid has high affinity to the surface of inorganic nanoparticles, conditioned by formation of chemical bonds with cationic centers on surface inorganic particles [21].

Inserting of β-styrylphosphonic acid during the synthesis of GdF_3 nanoparticles appeared to be impossible presumably, due to sediment of phosphonate gadolinium forming. Therefore we used a method of ligands exchange, in which dihexadecyldithiophosphate-ion adsorbed on the GdF_3 surface is partly substituted by β-styrylphosphonic-ion.

The content of Gd in compositions of nanoparticles before and after exchange ligands was determined by the complexometric titration method [22]. It is founded that in compositions of GdF_3, stabilized by ammonium dihexadecyldithiophosphate, a mass fraction of Gd is 30±1 %, and in composition of GdF_3, containing β-styrylphosphonic acid — 44±0.7 %. Increase of Gd content in compositions, containing β-styrylphosphonic acid, is presumably due to much smaller mass of aromatic ligand as compared to aliphatic surfactant.

According to [23, 24] bands, observed in IR spectra of β-styrylphosphonic acid, relates to vibrations aromatic groups -C=C- (1450, 1492, 1576, 1611 cm^{-1}), -P=O (1124–1241 cm^{-1}), -P–O(H) (957–999 cm^{-1}) (Fig. 3a). As bands specific for β-styrylphosphonic: aromatic -C=C- (3055 cm^{-1}) (Fig. 3b), -P=O (1266 cm^{-1}), -P–O- (948 cm^{-1}) and bands specific for dihexadecyldithiophosphate: -C–H- (2972, 2930 cm^{-1}) (Fig. 3b) are present in IR spectra of nanoparticles.

Inserting of β-styrylphosphonic acid in the nanoparticles material, notably improves their disperse in styrene and substantially increases transparency of polymer. It allows to get very transparent material with high content of nanoparticles (3, 5, 7, 10, 15 wt %).

On the basis of polystyrene — GdF_3 nanoparticles composites plastic scintillators were obtained, containing 0.02 wt % of 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP), 2 wt % of *p*-terphenyl and nanoparticles (0, 0.2, 0.5, 1, 3, 5, 7, 10, 15 wt. %). Their light yield was defined. As it seen in Fig. 4, the light yield of scintillators containing GdF_3 nanoparticles and stabilized only by ammonium dihexadecyldithiophosphate, rapidly decreases with an increase of the nanoparticles content in polymer, while decreasing of light yield of scintillators with GdF_3 nanoparticles, containing β-styrylphosphonic acid, is observed from the 5 wt. % of the nanoparticles.

4. Conclusions

Thus, in spite of stability in styrene dispersions of GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate, the polymerization of such colloidal solution results in visible nanoparticles aggregating starting from 0.5 wt. %. Use of the polymerizing component (β-styrylphosphonic acid) as a modifier of GdF_3 surface allowed to enter 7 wt. % of the nanoparticles and to maintain light yield at 90 % level relative to the standard scintillator, that is possible only in the case of high transparence of the polymeric material.

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Полімерний композит на основі полістиролу, що містить наночастинки фториду гадолінію

О.Ю.Ситнік, О.В.Свидло, П.М.Жмурін

Методом радикальної полімеризації стиролу в блоці отриманj полімерні композити, що містять наночастинки фториду гадолінію, стабілізовані дигексадецилдитіофосфатом амонію та β-стирилфосфоновою кислотою. Модифікація поверхні наночастинок β-стирилфосфоновою кислотою, здатною до сополімеризації зі стиролом, дозволяє істотно підвищити вміст наночастинок у полістирольному пластмасовому сцинтиляторі зі збереженням його сцинтиляційних властивостей.