Plastic scintillator enriched Gd-containing nanoparticles

O.V.Svidlo, P.N.Zhmurin, Yu.A.Gurkalenko

Institute for Scintillating Materials, STC "Institute for Single Crystals"
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

Polystyrene compositions containing GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate and fatty aromatic phosphonic acid (C_6H_5–$(CH_2)_n$–$PO(OH)_2$, n = 1, 2, 3) were obtained. It was shown that the nanoparticles surface modification by fatty aromatic phosphonic acids with high physical-chemical affinity to polystyrene significantly improves the nanoparticles dispersibility in polymer. The plastic scintillators with content of GdF_3 nanoparticles to 5 wt. % without significant loss of the light yield were obtained.

Получены полистирольные композиции, содержащие наночастицы фторида гадолиния, стабилизированные дигексадецилдитиофосфатом аммония и жирно-ароматической фосфоновой кислотой (C_6H_5–$(CH_2)_n$–$PO(OH)_2$, n = 1, 2, 3). Показано, что использование в качестве модификатора поверхности жирно-ароматических фосфоновых кислот, обладающих высоким физико-химическим сродством к полистиролу, приводит к существенному улучшению диспергируемости наночастиц в полимере. Получены пластмассовые сцинтилляторы с содержанием наночастиц GdF_3 до 5 масс % без существенной потери светового выхода.

Пластмасовий сцинтилятор, збагачений гадолінійвмісними наночастинками. *О.В.Свидло, Ю.О.Гуркаленко, П.М.Жмурін.*
Отримано полістирольні композиції, що містять наночастки фториду гадолінію, стабілізовані дигексадецилдитіофосфатом амонію та жирно-ароматичною фосфоновою кислотою (C_6H_5–$(CH_2)_n$–$PO(OH)_2$, n = 1, 2, 3). Показано, що використання в якості модифікатора поверхні жирно-ароматичних фосфонових кислот, що володіють високою фізико-хімічною спорідненістю до полістиролу, призводить до істотного поліпшення диспергування наночастинок у полімері. Одержано пластмасові сцинтилятори з вмістом наночастинок GdF_3 до 5.0 мас % без істотної втрати світлового виходу.

1. Introduction

Gd-loaded organic scintillators are effective materials for registration of thermal neutrons, solar and atmospheric neutrino. Among organic scintillators the plastic scintillators take a special place due to following reasons: ease of use, a relatively high scintillations efficiency, low response time, possibility of composition modification, low toxicity and high fire safety [1, 2].

For many experiments in high energy physics, particularly for neutrino registration, the plastic scintillators are required with several percent's level of gadolinium ions content of general mass of polymer. Gadolinium inorganic salts [3, 4], the complexes of gadolinium compounds [5, 6] and gadolinium carboxylates [7, 8] well soluble in an initial monomer are usually used as additives. But, as a rule, the plastic scintillators obtained in such a way are not stable in time, dyed, are not contained a sufficient

amount of gadolinium, and have a considerably low light yield. In recent years different methods are developed for synthesis of hydrophobic nanoparticles of lanthanide compounds (fluorides, oxides) which can be dispersed in non-polar organic environments [9–14]. It provides a possibility to get Gd-loaded polymer composites by the method of bulk polymerization when the nanoparticles inserted directly in a monomer before polymerization process.

Requirement of enriched by gadolinium plastic scintillators is constantly growing. Therefore, development of nanoparticles surfaces modification methods, which provide the maximum increase of Gd-nanoparticles dispersion in a polymeric base of the plastic scintillator with maintenance its scintillations properties, is an important technological goal.

This work is devoted to development of methods of Gd-containing nanoparticles surfaces modification that favor increasing their dispersibility in the polymer environment in order to obtain gadolinium-enriched plastic scintillators. The main criterion for efficiency of the nanocrystals introduction is the saving of the composite scintillator light yield at the maximum content of GdF_3 nanoparticles.

2. Experimental

In our study we used the following reagents: benzyl chloride (Sigma-Aldrich, 99.0 %), 2-phenylethyl bromide (Sigma-Aldrich, 98.0 %), 3-phenylpropyl bromide (Sigma-Aldrich, 98.0 %), 1-hexadecanol (Merck, for syntheses), phosphorus pentasulphide (Merck, 98.0 %), dichloromethane (Merck, for liquid chromatography), hexane (Ukraine, 95.0 %), methanol (Ukraine, 99.0 %), $Gd(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, 99.9 %), sodium fluoride (Ukraine, 99.0 %), styrene monomer (Ukraine, 99.0 %, distillation), toluene (Ukraine, 99.0 %), isopropanol (Ukraine, ≥97.0 %), triethylamine (Ukraine, ≥99.0 %), ammonia solution (Ukraine, 25.0 %), 2,2′-azobis(2-methylpropionitrile) (Sigma-Aldrich, 98.0 %), 1,4-bis(5-phenyloxazol-2-yl) benzene (Aldrich, 98.0 %), *p*-terphenyl (Merck, 98.0 %).

Obtained substances were investigated by IR spectroscopy using a Fourier IR Spectrophotometer SPECTRUM ONE (Perkin Elmer).

Confirmation of the structure of synthesized phosphonic acids was carried out by NMR spectroscopy. ^{1}H NMR spectrums were recorded on VARIAN Mercury VX-200

(200 MHz) spectrometer in dimethyl sulfoxide ($DMSO_6$) solution (internal standard — tetramethylsilane).

Light yield of polystyrene scintillators was measured by a scintillation spectrometer. It consisted of Hamamatsu R1307 photomultiplier and a charge-digit convertor LeCroi 2249A. Radionuclide Bi–207 was used as an electron source.

Morphology of the nanoparticles powders was characterized with a translucent electron microscope EM-125 (Selmi, Ukraine).

Ammonium dihexadecyldithiophosphate was synthesized according to the method described in [15]. According to the method, P_2S_5 and 1-hexadecanol were heated at 75°C for 3 h. The resulting suspension was cooled to the room temperature, then dissolved in dichloromethane and filtered. The solvent was distilled, the residue added into hexane, and ammonia was bubbled through the solution. The resulting precipitate was filtered and dried to the room temperature (M.p. 112–115°C).

Fatty aromatic phosphonic acid of general formula (C_6H_5–$(CH_2)_n$–$PO(OH)_2$ ($n = 1$–3) was prepared by alkylation of triethyl phosphite corresponding to phenylalkyl halide (the Michaelis-Arbuzov reaction) followed by hydrolysis of the resulting ester (Scheme 1).

The general method of C_6H_5–$(CH_2)_n$–$PO(OH)_2$, ($n = 1$–3) obtaining is as follow. $P(OEt)_3$ (30.0 mmol) and C_6H_5–$(CH_2)_n$–Hal (10.0 mmol) were refluxed for 16 h, after excess of triethyl phosphite was distilled
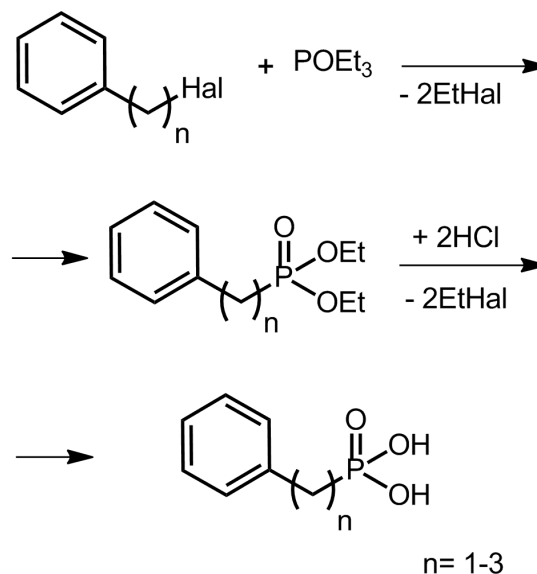
Scheme 1. Synthesis of fatty aromatic phosphonic acid C_6H_5–$(CH_2)_n$–$PO(OH)_2$, ($n = 1$–3).

and 200.0 ml of 20 % aqueous HCl solution was added to resulting ether, heated to reflux and held for 24 h. After that the solution was cooled to the room temperature, the resulting solid was filtered and purified by recrystallization.

Phenylmethyl phosphonic acid. The product was purified by recrystallization from a mixture of hexane/acetone (1:4).Yield was 70.0 %, it was white powder, m.p. = 172–174°C. Elemental analysis was the following: calculated for $C_7H_9PO_3$: C, 48.85; H, 5.27; O, 27.89; P, 18.00; found: C, 48.80; H, 5.23; O, 27.87; P, 18.06. ^{1}H NMR (200 MHz, DMSO–d_6): δ 7.34–7.08 (*m*, 5H, C_6H_5), 2.92 (*d*, *J* = 21.4 Hz, 2H, POH), 2.49 (*dd*, *J* = 5.8, 4.0 Hz, 2H, CH_2).

2-Phenylethyl phosphonic acid. The product was purified by recrystallization from a mixture of hexane/methanol (1:4). Yield was 63.0 %, it was white powder, m.p. = 146–147°C. Elemental analysis was the following: calculated for $C_8H_{11}PO_3$: C, 51.62; H, 5.96; O, 25.79; P, 16.64; found: C, 51.57; H, 6.06; O, 25.72; P, 16.58. ^{1}H NMR (200 MHz, DMSO–d_6): δ 7.47–6.99 (*m*, 5H, C_6H_5), 2.74 (*d*, *J* = 8.1 Hz, 2H, CH_2), 2.59–2.39 (*m*, 2H, POH), 1.82 (*d*, *J* = 17.5 Hz, 2H, CH_2).

3-Phenylprophyl phosphonic acid. The product was purified by recrystallization from H_2O. Yield was 52.0 %, it was white powder, m.p. = 124–125°C. Elemental analysis was the following: calculated for $C_9H_{13}PO_3$: C, 54.00; H, 6.55; O, 23.98; P, 15.47; found: C, 53.92; H, 6.50; O, 24.00; P, 15.52. ^{1}H NMR (200 MHz, DMSO–d_6): δ 7.44–6.97 (*m*, 5H, C_6H_5), 2.61 (*t*, *J* = 7.4 Hz, 2H, CH_2), 2.54–2.34 (*m*, 2H, POH), 1.74 (*d*, *J* = 8.9 Hz, 2H, CH_2), 1.57–1.27 (*m*, 2H, CH_2).

The GdF_3 nanoparticles were obtained by method of chemical precipitation in the presence of ammonium dihexadecyldithiosposhate in methanol/water. There the solution of ammonium dihexadecyldithiophoshate (0.95 mmol) and NaF (3.0 mmol) in methanol/water was heated to homogenization. Solution of $Gd(NO_3)_3 \cdot 6H_2O$ (1.33 mmol) in water was added dropwise and then cooled to the room temperature. The precipitate was separated by centrifugation and washed subsequently with water and methanol. The particles were further purified by dispersing in dichloromethane and precipitating by addition of isopropanol. After separation by centrifugation, the particles were dried on P_2O_5 in
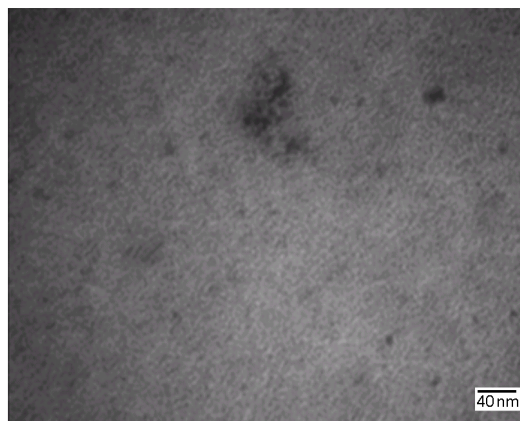

Fig. 1. TEM pictures of GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate.

vacuum for 48 h. Obtained GdF_3 nanoparticles, can be dispersed in non polar solvent such as toluene, dichloromethane and styrene.

The nanoparticles of GdF_3 containing fatty aromatic phosphonic acid were prepared by mixing GdF_3 nanoparticles modified by ammonium dihexadecyldithiophosphate with corresponding fatty aromatic phosphonic acid and triethylamine in dichloromethane during twenty-four hours and the following precipitating them by isopropanol.

Polymeric compositions were obtained by radical bulk polymerization of styrene with the dispersed nanoparticles using 2,2′-azobis(2-methylpropionitrile) initiator (0.4 wt. % of the monomer) at 65°C during for 72 h.

3. Results and discussion

Introduction of surfactant (a surface modifier) in the synthesis process is an effective method of regulating the size of the nanoparticles formed and it substantially reduces tendency of the nanoparticles aggregation in the non-polar medium. Phosphor and thiophosphoric acids and their derivatives containing in their structures the long hydrocarbon radicals are widely used as surfactants. Their presence ensures the dispersibility of the nanoparticles in organic solvents. Furthermore, phosphoric and thiophosphoric acids, and their derivatives have high affinity to the surface of inorganic nanoparticles, due to formation of chemical bonds with cationic sites on the surface of the inorganic particles [16].

To obtain the inorganic nanoparticles capable of dispersing in toluene a compound
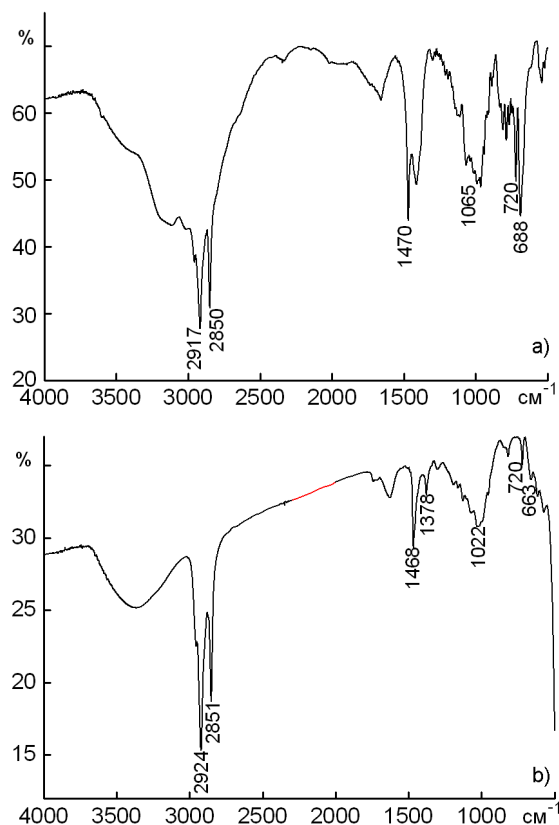
Fig. 2. IR spectra of ammonium di-hexadecyldithiophosphate (a) and GdF_3 nanoparticles stabilized by ammonium di-hexadecyldithiophosphate (b).
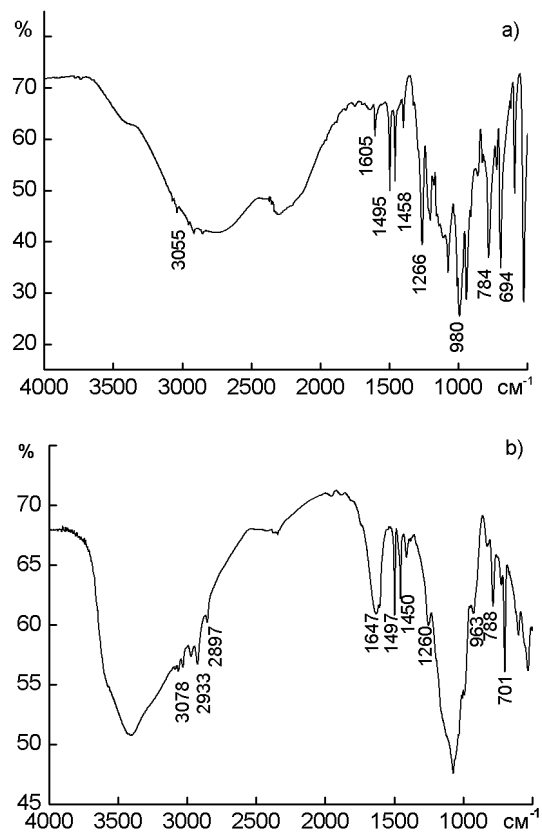

Fig. 3. IR spectra of phenylmethyl phosphonic acid (a) and GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate and phenylmethyl phosphonic acid (b).

of O,O-dialkyldithiophosphate type was used as a surfactant in the studies [10–13, 17]. Therefore to obtain the GdF_3 nanoparticles dispersion in styrene we synthesized GdF_3 nanoparticles with surface modified by ammonium dihexadecyldithiophosphate.

As can be seen in Fig. 1, the obtained nanoparticles have about 1–5 nm size, and they are uniformly distributed across the substrate.

IR spectra of ammonium di-hexadecyldithioposhate and surface modified GdF_3 nanoparticles with ammonium di-hexadecyldithiophosphate are shown in Fig. 2. The both spectra 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. 2a) and 1468 cm^{-1} (Fig. 2b) bands correspond to deformation vibrations of C–H groups. The bands at 2917 cm^{-1} and 2850 cm^{-1} (Fig. 2a), 2924 cm^{-1} and 2851 cm^{-1} (Fig. 2b) correspond to the stretching vibrations of C–H groups and the band of low intensity at

720 cm^{-1} (Fig. 2a,b) — to the pendulum vibrations of (-CH$_2$) group [19].

Bands, characterizing vibrations of (P)–O–C, at 1064 cm^{-1} (Fig. 32a and 1022 cm^{-1} (Fig. 2b), — P=S at 688 cm^{-1} (Fig. 2a) and 663 cm^{-1} (Fig. 2b) (relative intensity decreases in the adsorbed state), displaced toward the low frequency for adsorbed surfactant, which determined, presumably, by influence of coordination of dithiophosphate-ion with the ions of gadolinium on the GdF_3 nanoparticles surface.

The obtained GdF_3 nanoparticles were used for preparation of sols in styrene monomer with 0.2, 0.3, 0.5, 0.7, 1.0, 1.5 and 2.0 wt.% concentrations of the nanoparticles with further polymerization. It was founded, that when the content of additives is greater than 0.5 wt. % after polymerization the polymer samples lose their transparency. This demonstrates that, despite the ability of GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate produce highly concentrated form of dispersion in the monomer, in the poly-
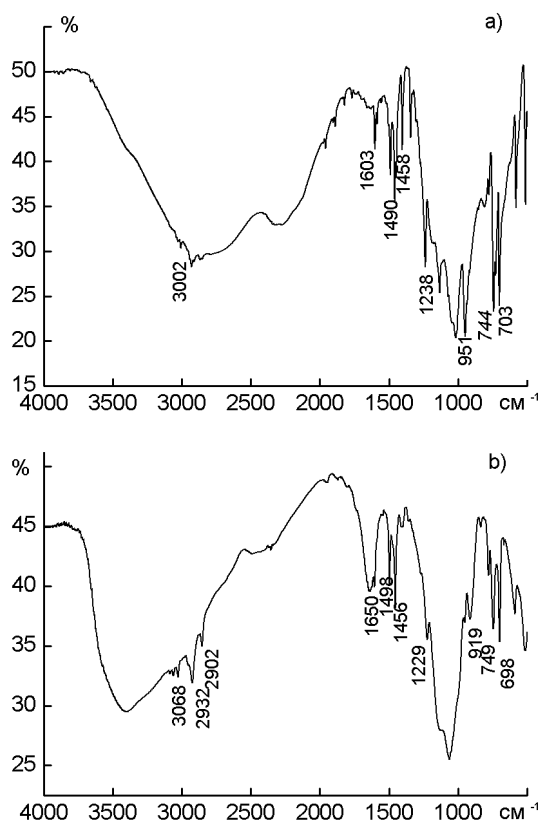
Fig. 4. IR spectra of 2-phenylethyl phosphonic acid (a) and GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate and 2-phenylethyl phosphonic acid (b).
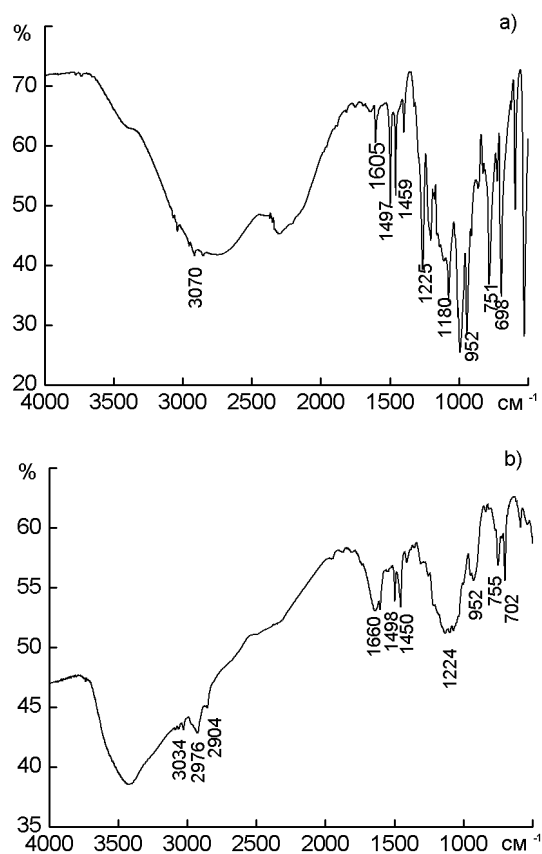

Fig. 5. IR spectra of 3-phenylpropyl phosphonic acid (a) and GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate and 3-phenylpropyl phosphonic acid (b).

mer they are only slightly dispersed. Dispersibility of the nanoparticles in the polymeric volume can be increased by using an additional component which has a strong chemical affinity to the polymer. Arene are compatible with polystyrene due to similarity of the molecular structure. Fatty aromatic phosphonic acids derivatives of general formula $(C_6H_5–(CH_2)_n–PO(OH)_2$, ($n = 1$, 2, 3) are selected as such compounds because they contain phenylalkyl group similar to the structure of polystyrene monomer unit. Moreover, as indicated above, phosphonic acid has high affinity to the surface of inorganic nanoparticles, conditioned by formation of chemical bonds with cationic centers on surface inorganic particles.

Preparation of GdF_3 nanoparticles modified by fatty aromatic phosphonic acid by its direct introduction during the synthesis was impossible, because in this case precipitate of gadolinium phosphonate is apparently formed. Therefore we used the method of ligands exchange [20,21], in which dihexadecyldithiophosphate-ion adsorbed on

GdF_3 surface is partly substituted by the phosphonic-ion.

The content of Gd in compositions of the nanoparticles before and after ligands exchange was determined by the complexometric titration method [22]. It was found that in compositions of GdF_3 stabilized by ammonium dihexadecyldithiophosphate a mass fraction of Gd was 15±1 %, in composition of GdF_3 containing phenylmethyl phosphonic acid — 18±0.7 %, in composition of GdF_3 containing 2-phenylethyl phosphonic acid — 19±0.3 % and in composition of GdF_3 containing 3-phenylprophyl phosphonic acid — 19±0.1 %.

IR spectrum of a phenylmethyl phosphonic acid is shown Fig. 3a. The bands at 1605 cm^{-1}, 1495 cm^{-1} and 1458 cm^{-1} correspond to the stretching vibrations of –C=C– groups. The band at 3050 cm^{-1} corresponds to the stretching vibrations of C–H aromatic groups and the bands of high intensity at 784 cm^{-1} and 694 cm^{-1} correspond to the non-planar deformation vibra-

tions of five adjacent hydrogen atoms in benzene ring [23]. According to authors of [23], the band of weak intensity at 1266 cm^{-1} is characteristic of the stretching vibrations of –P=O group [19, 23]. Probably, 997 cm^{-1} and 980 cm^{-1} bands correspond to the vibrations of –P–O(H) group [24]. The bands specific for phenylmethyl phosphonic, the bands –C=C– (3002 cm^{-1}), –P=O (1260 cm^{-1}), –P–O(H) (963 cm^{-1}) are present in the IR spectra of the nanoparticles modified by phenylmethyl phosphonic acid (Fig. 3b). Relative intensity of the bands decreases in the adsorbed state [25].

The bands observed in IR spectra of 2-phenylethyl phosphonic acid (Fig. 4a) are related to the stretching vibrations of aromatic groups C–H (3002 cm^{-1}), –C=C– (1603, 1490, 1458 cm^{-1}), C–H groups mono-substituted benzene ring (744 and 703 cm^{-1}), –P=O (1238 cm^{-1}) and –P–O(H) (951 cm^{-1}1). The bands specific for 2-phenylethyl phosphonic, the bands –C=C– (3068 cm^{-1}), –P=O (1229 cm^{-1}), –P–O(H) (919 cm^{-1}) are present in the IR spectra of the nanoparticles modified by 2-phenylethyl phosphonic acid (Fig. 4b).

IR spectrum of 3-phenylpropyl phosphonic acid (Fig. 5a) contains bands of aromatic groups C–H (3070 cm^{-1}), –C=C– (1605, 1497 and 1456 cm^{-1}), C–H groups of mono-substituted benzene ring (751 and 700 cm^{-1}), –P=O (1250–1180 cm^{-1}) [23] and –P–O(H) (952 cm^{-1}). The bands specific for 3-phenylpropyl phosphonic bands –C–H– (3034 cm^{-1}), –P=O (1224 cm^{-1}) and –P–O(H) (948 cm^{-1}) are present in the IR spectra of nanoparticles modified by 3-phenylpropyl phosphonic acid (Fig. 5b).

It was found that surface modification of GdF$_3$ nanoparticles by fatty aromatic phosphonic acid component having a high affinity to polystyrene matrix significantly improves their dispersibility in styrene. It allows to obtain the transparent material with high content of the nanoparticles (3, 4, 5, 7 wt. %). Thus on the basis of GdF$_3$ nanoparticles modified by phenylmethyl phosphonic acid we obtained the transparent polystyrene composite containing to 3.0 wt. % of the nanoparticles. Basing on GdF$_3$ nanoparticles modified by 2-phenylethyl phosphonic acid — it was obtained the composite containing to to 5.0 wt. % and basing on GdF$_3$ nanoparticles modified by 3-phenylpropyl phosphonic acid — the composite with up to 7.0 wt. % of the nanoparticles. Apparently, the elongation of aliphatic moiety in the molecule of fatty aro-

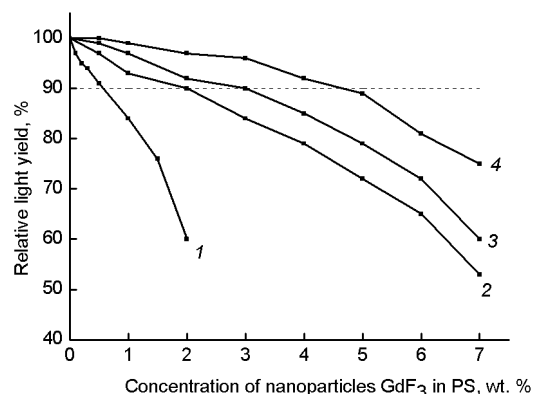
Fig. 6. Relative light yield of Gd-activated scintillators vs. nanoparticles content: *1* — GdF$_3$ nanoparticles stabilized by ammonium dihexadecyldithiophosphate; *2* — GdF$_3$ nanoparticles stabilized by ammonium dihexadecyldithiophosphate and phenylmethyl phosphonic acid; *3* — GdF$_3$ nanoparticles stabilized by ammonium dihexadecyldithiophosphate and 2-phenylethyl phosphonic acid; *4* — GdF$_3$ nanoparticles stabilized by ammonium dihexadecyldithiophosphate and 3-phenylpropyl phosphonic acid.

matic phosphonic acid (C_6H_5–$(CH_2)_n$–$PO(OH)_2$, n = 1, 2, 3) also improves dispersibility of the nanoparticles modified with such surfactants in polystyrene.

On the basis of polystyrene — GdF$_3$ nanoparticles composites, plastic scintillators were obtained, which contain 0.02 wt. % of 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP), 2.0 wt % of *p*-terphenyl and nanoparticles (0, 0.2, 0.3, 0.5, 1.0, 1,5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 wt %). The main criterion of efficiency of the nanoparticles insertion was the maximum content of the nanoparticles in the plastic scintillator, while maintaining its light yield at 90 %.

Dependence of relative light yield of the plastic scintillators on GdF$_3$ nanoparticles concentration is presented in Fig. 6. As it seen in Fig. 6, the light yield for scintillators containing GdF$_3$ nanoparticles stabilized only by ammonium dihexadecyldithiophosphate rapidly decreases with increase of the nanoparticles content in the polymer. At the same time decreasing the relative light yield below 90 % of the plastic scintillators with GdF$_3$ nanoparticles modified by phosphonic acid C_6H_5–$(CH_2)_n$–$PO(OH)_2$, (n = 1, 2, 3) occurs only when the concentration of the nanoparticles is greater than 2, 3 and 5 wt. % for n = 1, 2 and 3, respectively.

These results allow to suggest that further increase of the number of methylene

units in the molecule of fatty aromatic phosphonic acid $(C_6H_5-(CH_2)_n-PO(OH)_2$, $n = 1-3$) will lead to an improvement in the nanoparticles dispersibility in the polymer. It will allow to obtain the plastic scintillators with high content of gadolinium without significant loss of the light yield.

4. Conclusions

In spite of the ability of GdF_3 nanoparticles stabilized by ammonium dihexadecyldithiophosphate to form the transparent highly concentrated dispersion in the monomer, their dispersion in polystyrene is rather low (up to 0.5 wt. %). Using a component which has high physical-chemical affinity to polystyrene (fatty aromatic phosphonic acid $C_6H_5-(CH_2)_n-PO(OH)_2$, $n = 1-3$) as a modifier of GdF_3 surface allowed to introduce 5.0 wt % of the nanoparticles in the composite scintillator maintaining the light yield at 90 % level relative to the standard plastic scintillator.

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