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DESIGN OF NEW POLYMERS TO IMPROVE RADIATION STABILITY OF PLASTIC SCINTILLATORS

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ABSTRACT

Diffusion enhancers have been used to increase the radiation stability of scintillators. There is a danger that such additions will also allow the scintillation dyes to diffuse out of the matrix. Covalent bonding of the dyes into the matrix would eliminate any luminophore migration. We have demonstrated that dyes with vinyl and divinyl groups can be successfully bonded into a styrene matrix. Both primary and secondary luminophores have been bonded into the matrix and in several cases they have been compared with similar luminophores without the vinyl groups in otherwise identical compositions. In general the bonding does not greatly affect either the radiation stability of the composition or its light output, but is therefore proven to be an acceptable method of preventing luminophore migration. Scintillators with a base of aromatic or alicyclic epoxy resins have also been made with bonded luminophores. In these compositions the bonding is accomplished by using luminophores with one or two amine groups or epoxy groups. When using the amines, they are first prereacted with the epoxy resin and the modified epoxy is then cured with hexahydrophthalic anhydride or trimethoxyboroxine. The emission and absorption spectra of many of these reactive luminophores are given, along with the light outputs and radiation stability of the resulting scintilators.

Plastic scintillators are often used in high energy particle physics, especially as the sampling element in calorimeters.[1] Modern colliding beam experiments

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subject scintillators to higher doses of radiation than ever before. Currently available plastic scintillators are susceptible to radiation damage and their light yield decreases with exposure time. A radiation hard plastic scintillator can be defined as a scintillator that can recover a substantial amount of its light output in a short time after being irradiated. In an attempt to accelerate the annealing period and reduce permanent damage, plasticizers have been added to the polymer base to enhance chain mobility.[2] Unfortunately, this approach may give rise to a new drawback. The dopants may now also have higher mobility and diffuse out of the polymer matrix. In order to avoid this problem, the dopants could be covalently bound to the polymer matrix.[3]

The introduction of molecules of luminophores into polymer chains sometimes can increase resistance of luminophores[4] or polymers[5] to ultra-violet light. Let us assume that the covalent bonding of luminophoric dopants with the polymer matrix of a scintillator can also increase its stability toward ionizing radiation. There are literature data[6,7] concerning the introduction of biphenyl, naphthalene and p-terphenyl into a polymer chain by copolymerization of their vinyl derivatives with styrene. The aforementioned authors observed some increase in radiation stability of copolymers of styrene or 2,4-dimethylstyrene with vinylbiphenyl in comparison with homopolymers which have no fragments of biphenyl.

An investigation of the radiation stability of scintillators with a matrix of copolymers of styrene and 12 different fluorescent compounds has been made. The fluorescent monomers contained one or two unsaturated groups, such as vinyl, methacryl, -allyl. The 4'-vinyl-9, 10-diphenylanthracene has been obtained from 9, 10-anthraquinone, phenylmagnesiumbromide and 4-magnesiumbromstyrene. Methacryl- and allylderivatives of dyes have been obtained by treatment of aminoderivatives of dyes with chloranhydride methacrylic acid or allylchloride, respectively. Other new dyes have been synthesized by methods given in reference 3.

In table 1 we give the chemical structure of the fluorescent monomers and the wavelengths of the maxima in their absorbance and fluorescence spectra in styrene solution. The spectral properties of most of these compounds make them suitable for use as secondary dopants in polystyrene scintillators. However, some of them, e.g. 4-vinyl-p-terphenyl, can be used as primary dopants.

In order to understand the influence of the covalent bonding of luminophoric dopants with polystyrene matrix, whenever possible we compared the transmittance and fluorescence spectra and the light yields of polystyrene scintillators with dopants of similar structure but without the presence of a vinyl group.

In table 2, the composition and characteristics of the resulting scintillators are shown. In these compositions p-terphenyl (PTP) or 2-(4-biphenylyl)-5-(4-tert-butylphenyl)- 1,3,4-oxadiazole (BPBD) are used as primary dopants.

TABLE 1

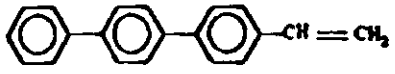
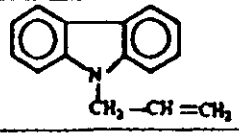
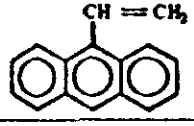
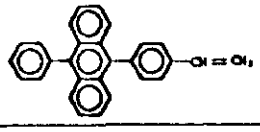
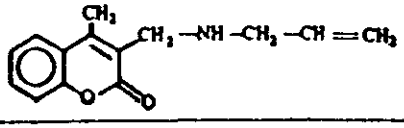
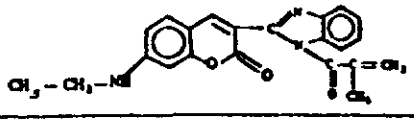
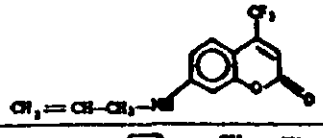
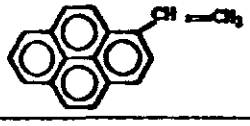
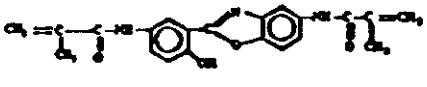
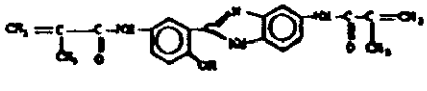
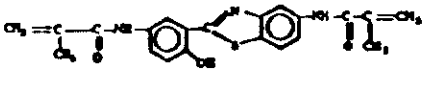
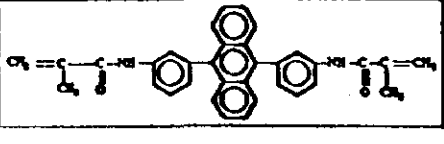
#	Luminophore		Absorption	Fluoresence
	Structure	Name	λ_{max} nm	λ^{fl}_{max} nm
1		VPT	305	355,370
2		Al K	330,350	365,380
3		VA	350,375,390	415,430
4		VDPA	355,375,390	420,435
5		Al-C-1	380	440
6		N-Al-C	440,450	400,510
7		Al-C-2	375	445
8		VPy	325,340	320,240
9		DMBO	325,355	525
10		DMBT	320,350	510
11		DNBT	330,370	540 (Weak)
12		DMA	355,370,385	415,475

Table 2

#	Primary dopants	Secondary dopants 0.02%	λ^{fl}_{max}, in nm	Light output in % of BC408: Before irrad.	Light output after 10Mrad: after 3 days	Light output after 10Mrad: after anneal	Output in % of before: after 3 days	Output in % of before: after anneal
1	1.25% pT	VPy	398	28	9	11	32	39
2	1.25% pT	VA	420,450	65	14	22	22	34
2'	1.25% pT	Anthracene	405,425	31	9	17	29	55
3	1.25% pT	VDPA	430	83	20	29	24	35
3'	1.25% pT	DPh Anthracene	430	80	14	22	18	28
4	1.25% pT	DMA	425	78	17	25	22	32
5	1.25% pT	Al-K	375	60	9	13	15	22
6	1.0% BPBD	Al-C-1	430	46	9	16	20	35
7	10% BPBD	Al-C-2	440	78	11	25	14	32
7'	10% BPBD	C 500	440	62	9	20	15	32

Comparing the two systems, we can see that the fluorescent properties and light output of each are similar before irradiation. The only exception is the copolymer of styrene with 9-vinylanthracene (#2). Its light yield is twice as much as the light yield of the polystyrene scintillator with anthracene (#2') as the secondary dopant. The increased fluorescence quantum yield of the 9-alkyl derivatives of anthracene in comparison with the yield of anthracene[7] is the explanation of this difference. It would have been better to have used 9-methyl- or 9-ethyl anthracene as secondary dopants for a more correct comparison.

A decrease of transmittance and light yield is observed after gamma-irradiation to 10 Mrad in a nitrogen atmosphere. Immediately after irradiation, the light yield is one-third to one-sixth what it was before. After annealing in oxygen atmosphere (7 days, 160 psig) the light yield is one-half to one-fourth as much as it was before. If we compare bound and unbound luminophore systems using the data from the last 2 columns of table 2, we see that in the case of systems 2 and 2' the bound luminophore retains less of its light output after irradiation and annealing. In the case of systems 7 and 7' the amount retained is about the same. In the case of systems 3 and 3' the bound luminophore retains more of its light output.

Luminophoric dopants with two methacrylic groups are very interesting because these compounds can produce cross-linked copolymers after polymerization with styrene. The advantage of cross-linked copolymers is that they may make possible the use of large concentrations of diffusion enhancers. Such concentrations would otherwise cause a softening of linear polystyrene.

In table 3 are listed two dimethacrylic compounds and one methacrylamide compound with green fluorescence. Also shown are the fluorescence maxima, the relative brightness, and the decay time of copolymers of styrene with these luminophores. The brightness of the copolymers has been measured in

Table 3

#	LUMINOPHORE 0.02%	λ_{max} nm	Brightness In % of K-27	Decay Time ps
1	K - 27	495	100	11.8
2	DMBI	500	38	5.2
3	DMBO	530	44	5.4
4	N Al C	505	74	7.1

comparison to the brightness of solid solutions of the dye K27 in polystyrene when illuminated by the light from scintillator SCSN38. In spite of lower brightness, these copolymers are interesting as green dopants for scintillator fibers. They have short decay times (5.2-7.1 ns compared to 11.8 n sec for K27), and big Stokes shifts (150-170 nm).

We have studied other scintillating compositions consisting of styrene copolymerized with 1% of reactive luminophores (see table 1) as primary dopants and .02% of the non-reactive luminophores BBQ or K27 as secondary dopants. Table 4 shows the compositions and some properties of these scintillators.

TABLE 4

Light Output Measurements of Copolymers of Styrene and Vinylluminophores

	Primary Dopants 1%	Secondary Dopants .02%	Fluorescence λ_{max} in nm	Light Output in % of BC 408				
				Before Irradiation	After Irradiation and Air Anneal			
					10 Hours	30 Hours	6 Days	30 Days
1	VPy	BBQ	405,490	21	6.5	7	9	12
2	VA	K27	430,470,495	19	4.6	5.3	6.8	11
2'	Anthracene	K27	410,470,495	15	5.6	6.3	7.5	10
3	VDPA	K27	440,470,495	36	11	12	17	22
3'	Diphenylanthracene	K27	430,470,495	38	14	17	22	29
4	DMA*	K27	435,470,490	30	27	33	66	66
5	Al K	BBQ	380,490	33	8	10	13	17
6	Al - C-2	K27	435,460,495	24	2.6	3.1	5.3	5.3
6'	C 500	K27	460,495	25	1.8	2.3	2.3	7.8

* Concentration of DMA = .5%

As we did with the systems in table 2, we have compared the light output before and after irradiation of scintillators based on copolymers of styrene and reactive primary dopants with the light output of scintillators based on solid solutions in polystyrene of dopants of similar structure. We have obtained the best light output before irradiation (38% of BC408) and the best light output after irradiation and 33 days annealing (76% of the before irradiation measurement) for the composition with diphenylanthracene as the primary dopant. By comparing the data from sample 2 with 2', and sample 3 with 3', and sample 6 with 6', we conclude that the covalent bonding of the primary dopants with the polymer matrix does not increase the light output. The data show that it might cause a slight decrease in the light output retained after irradiation and annealing. Note that the data for bound secondary dopants showed mixed results.

Since no large deleterious effects were seen with either bound primary or secondary dopants we can conclude that these reactive luminophores are suitable for use in diffusion enhanced systems where unbound luminophores might migrate out of the base plastic.

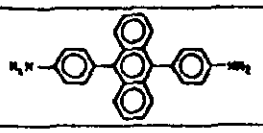
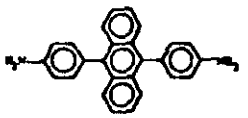
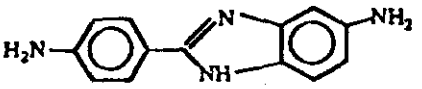
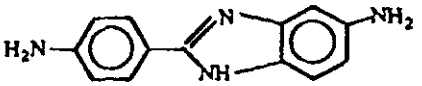
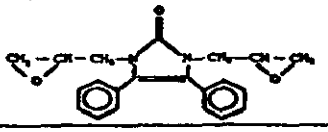
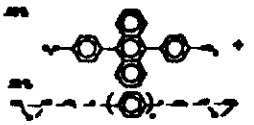
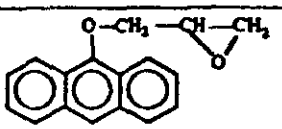
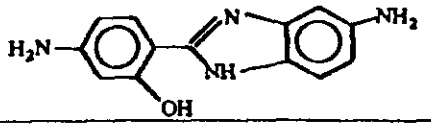
We have also investigated new polymer base epoxy resins and new fluorescent compounds containing functional groups which are able to react with these resins. Dyes with one or two glycidyl groups have been synthesized by treatment of hydroxy- or aminoderivatives of dyes with epichlorhydrin by the method of reference 3. An epoxy system has the advantage of yielding polymers of various chemical structures just by changing the epoxy monomers and curing agents. Moreover epoxy polymers are highly crosslinked networks. This characteristic may facilitate the use of larger amounts of diffusion enhancers without making the scintillator too soft.

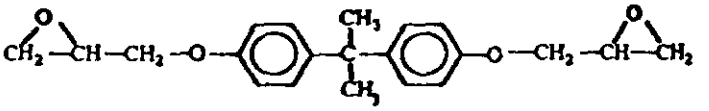
Two types of epoxy resins have been used. One with an aromatic structure, the diglycidylether of bisphenol-A (DER 332), and one with cycloaliphatic structure, (ERL-4234). Scintillators were made by dissolving luminophores having one or two glycidyl groups (see table 5) in the epoxy resins and curing with trimethoxyboroxine or hexahydrophthalic anhydride (HHPA). After curing, the luminophoric dopants should be covalently bound to the polymer matrix. The epoxy-epoxy reaction catalyzed by trimethoxyboroxine (TMBOX) produces more nearly colorless polymers.

A second method of introducing molecules of luminophores into polymer chains is to prereact epoxy resin with diaminoluminophores (table 5) by heating the mixture overnight at 110-120°C. From this process slightly yellow olygomers are usually obtained. Subsequently these olygomers are reacted with TMBOX (overnight at 90°C) or with HHPA (5-20 days at 90°C). We have found that the reaction of epoxy groups with HHPA may be accelerated by benzimidazole derivatives used as secondary dopants (samples 3,4,11 in table 5).

Also in table 5 the composition and some properties of the resultant scintillators are shown. These scintillators contain 1.5% p-terphenyl as primary

TABLE 5

#	Secondary Dopant .02%	Curing Agent	λ^{n}_{max} nm	Light Output in % of BC 408
1		TMBOX	470	37
2	 *	HHPA	460	14
3		TMBOX	450	28
4		HHPA	450	17
5	DPH Anthracene	TMBOX	420,440	40
6	0.02% DPhAnthracene + 0.02%	TMBOX	380 (shoulder) 420,440	54
7		TMBOX	405 (shoulder)	28
8	0.02% DPhAnthracene +	TMBOX	380 (shoulder) 420,440	51
9		TMBOX	380 (shoulder) 470	43
10		TMBOX	405,430	34
11		HHPA	455	14

Epoxy Resin 

Primary Dopant 1.5% pT

* .08%

dopant and 0.02% diamino- or diglycidyl luminophores as secondary dopants. In some cases we used two luminophores as secondary dopants. Diglycidyl ethers of dihydroxyquaterphenyl or dihydroxydiphenyloxadiazole efficiently absorb the emission of the primary dopant and fluoresce in the region of absorption of the secondary luminophores. Usually the light yield of epoxy polymer scintillators with two secondary dopants is higher than the light yield of scintillators with one secondary dopant of the same chemical structure as one of the two (compare the characteristics of samples 6,8,and 9 with those of samples 1 and 5 in table 5).

If we compare properties of copolymers with fragments of diaminoluminophores prepared by curing with TMBOX, with properties of copolymers prepared by curing with HHPA, we see that the light yield of the first type is higher than that of the second type, as table 5 shows.

The highest light yield (54% in comparison with BC408, sample 3) was obtained from the diglycidyl ether of bisphenol A using TMBOX as curing agent, PTP as primary dopant, and a diglycidyl derivative of quaterphenyl and diphenylanthracene as secondary dopants. Epoxy systems with light yields of 70% of BC408 have been reported.[2]

The epoxy polymers obtained from cycloaliphatic epoxy resins alone can not be used as scintillators because they have no aromatic links. To make scintillators from these epoxy polymers it is necessary to add large concentrations of naphthalene or other aromatic compounds.

Table 6 gives the composition and some characteristics of scintillators obtained from cycloaliphatic resins. HHPA as curing agent and 5-15% of naphthalene have been used in the preparation of these epoxy scintillators. Table 6 shows that the light yield of these epoxy scintillators is lower than the light yield of epoxy scintillators obtained from aromatic epoxy resins (table 5). We hope that the light yield of scintillators obtained from cycloaliphatic epoxy resins can be increased by increasing the concentration of naphthalene.

Two types of new scintillators obtained from modification of polystyrene and from epoxy polymers have been investigated in this work. The absorption, fluorescence and scintillation light yield characteristics before and after irradiation have been determined.

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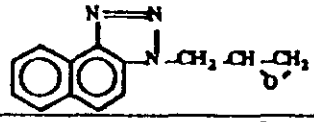
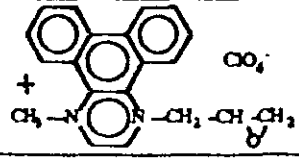
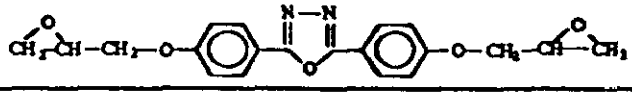
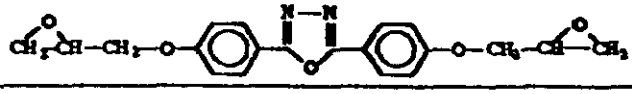
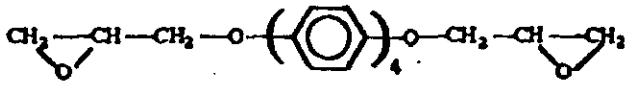
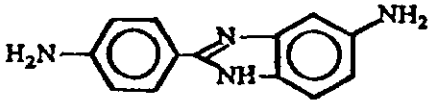
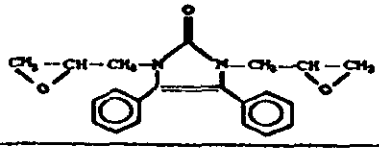
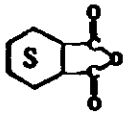
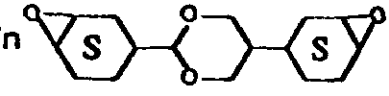
TABLE 6

#	Primary Dopant	Secondary Dopant, 0.02%	λ^{fl}_{max} in nm	Light Output in % of BC 408
1	1.5% pT 5 % N*	Tetraphenylbutadiene (TPhB)	430	9
2	1.5% pT 5% N*	0.02% TPhB + 	360 †, 430	13
3	1.5% pT 10% N*	0.02% TPhB + 	370 †, 430	11
4	5% pT	DPh Anthracene	420, 440	9
5	5% pT	0.02% DPhAnthracene + 	360 †, 420, 440	9
6	1.5% pT 15% N*	0.02% DPhAnthracene + 	360 †, 420, 440	13
7	1.5% pT 5% N*	0.02% DPhAnthracene +	360 †, 420, 440	11
8	1.5% pT		380 †	6
9	1.5% pT 10% N*		440	11
10	1.5% pT 5% N*		405†	9

* = Napthylene

† = shoulder

Curing Agent HHPA 

Epoxy Resin ERL 4234 

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