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Chapter 1

Introduction – Overview on Plastic and Inorganic Scintillators

Christophe Dujardin and Matthieu Hamel

Abstract Scintillators are materials that are able to emit photons when impinged with ionizing radiations. This family of materials is covered by both organic and inorganic structures, with some similarities but also with different photophysical processes occurring underneath. The scientific fields and communities are in fact rather separated, while it would benefit from more interactions. This book is mostly focused on plastic scintillators, which are polymer-based materials, and the purpose of this Chapter is to introduce and link them to well-known inorganic scintillators. In addition, hybrids materials are new developments based on inorganic nanocrystals in organic host. In such hybrid materials, a complex interplay occurs along the energy relaxation leading to the emission of light. Thanks to their chemical versatility, plastic scintillators can easily be modified. Whereas the first decades have seen their use as “all-purpose” detectors, the most recent developments afford specialization of the materials towards a given application. Thus, various modification stages are possible: the simplest is to tune its chemicals properties. In addition, this material is an optical device and complicated photophysical phenomena occur in the radiation/matter interaction volume. Finally yet importantly, current developments in artificial intelligence as well as highly sophisticated algorithms are used to overcome intrinsic limitations of plastics properties. This chapter thus gives a historical perspective on the development of plastic scintillators with a mention of past and current main actors. Then a discussion follows on the basic principles in plastic scintillation design. Their main properties are finally presented and compared with inorganic scintillators. Some of these properties will be barely discussed herein since they will be fully explained in dedicated chapters.

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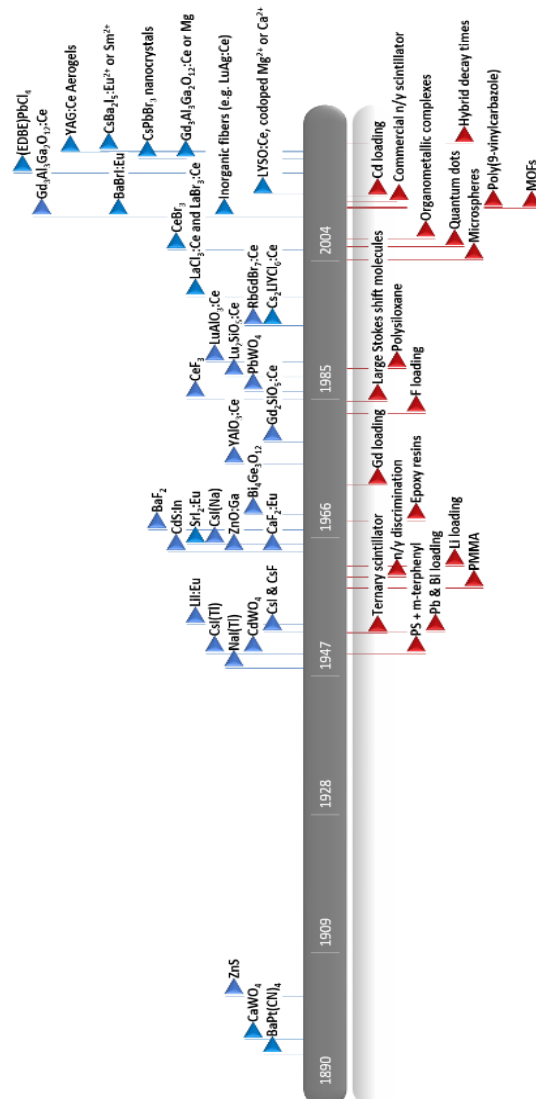
1.1 History of Scintillators

The first scintillator ever described was $\text{BaPt}(\text{CN})_4$ in the frame of x-ray detection in 1895. It was under the form as a powder, now called x-ray phosphor and played a major role in medical x-ray radiography. With the emergence of photomultipliers, the research on scintillating materials has been intensified. Thus, plastic scintillators (PSs) were first depicted in the literature by Marvin G. Schorr and Franklin L. Torney as early as 1950 [1], a few months only after their liquid equivalents were discovered [2, 3]. Regarding inorganic scintillators as single crystals, the main known compositions were discovered after the 1950s as depicted in [4].

This first plastic was composed of *m*-terphenyl dissolved in polystyrene¹. Rapidly various formulations appeared which highlighted the necessity to add a wavelength-shifter (i.e. a molecule that is able to absorb UV light from the primary fluorophore and emits at longer wavelengths) to the abovementioned binary mixture so as to afford better scintillation external efficiency, including the light extraction as mentioned by Pichat and Pesteil [5]. These discoveries lead to the commercial plastic formulations we currently know. In 1953, the first loading attempts with organometallics in the form of bismuth hexahydrobenzoate or triphenylmethyllead were published by the same French group, already with the aim of increasing the effective atomic number for gamma spectroscopy [6]. This scintillator modification is one of the hottest topic in the context of homeland security [7, 8], the other one is the pulse shape discrimination between fast neutrons and gamma rays [9, 10] which was first described by Frank D. Brooks in 1960 [11]. Concerning thermal neutrons (i.e. with kinetic energy in the range of 25 meV) detection, loading with dedicated elements allowing their capture appeared in the early sixties. Thus, lithium was described in a Russian patent [12] and boron in a British report, later on popularized in a paper from Anisimova [13], thanks to isopropenyl boron carbohydride. Gadolinium appeared a few years later in the form of gadolinium benzoyl acetate at low concentration (typically $\leq 0.2\%$ of Gd) [14]. Gamma spectroscopy and neutron detection with plastics will be fully described in dedicated chapters of this book. Some other application-driven but peculiar developments were also performed: fluorine loading for high-energy neutron detection [15-17], cadmium loading [18], hafnium [19], various lanthanides and actinides [20], etc. Various elements can thus be loaded into plastics. Selected developments for both inorganic and organic scintillators are summarized in Fig. 1.1.

¹ Topological representation and key information of these molecules is given in the Appendix section at the end of the book.

Fig. 1.1 Timeline of the main scintillator developments from 1890 to 2020 (illustrative only; for inorganics rather fast scintillators are considered)



Later, John B. Birks published the first book on the principle of scintillation counting in 1964, covering notably the latest developments and use of plastics and inorganics [21]. During these first fifteen years, plastics were extensively studied with the aim to find the best composition in terms of scintillation efficiency, decay time, chemical stability, etc. It is noteworthy that the well-known combinations of fluorophores, e.g. *p*-terphenyl/POPOP or PPO/POPOP were discovered at this time, and

more details will be given in the following sections. Nowadays important developments are still performed as can be seen in the increasing number of publications talking about plastic scintillator modifications (Fig 1.2).

Soon after the discovery of plastic scintillators, physics and chemical research were followed by their industrial production. The Cold War probably took a key role as it involved important needs in the context of nuclear and radiological detection and radioprotection of the workers involved in the preparation of nuclear weapons. The two Blocs thus independently created their own facilities to cover them. Several different companies emerged for the Western Bloc: *Pilot Chemicals* (USA, est. 1951), *National Radiac INC.* (Sintilon material, USA, before 1956 [22]), *Bicron* (USA, est. 1969), *Koch Light* (UK and USA, before 1969), and *Nuclear Enterprises Ltd.* (Scotland). Plastic scintillator NE 102 (NE standing for *Nuclear Enterprises*) was cited in as early as 1959 [23]. Naton scintillators (*Nash & Thompson*, UK) appeared in the first part of the 1960s. Later on, the Pilot-*x* references appear in the *Nuclear Enterprises* catalog. *Altulor* (France, 1957) and *Polivar* (Italy) were involved in the preparation of PMMA-based PSs, mostly for CERN experiments during the years 1985–1990. Some old catalog front covers can be seen in Fig 1.3. From the Eastern Bloc, two main institutes were created. First is the *Institute for High-Energy Physics* (IHEP, USSR, 1963). The research and development program of plastic scintillators started in the 1970s from the initiative of V. Rykalin. In the beginning, the technology of manufacturing PSs by the method of large-block thermal polymerization (SC-2xx series) followed by mechanical treatment and polishing was settled. Then extruded plastics (SC-3xx series) were extensively studied. Other trade codes from IHEP exist under the form PSM-xxx series. For example, PSM-115 (an injection-molded plastic) was used in HERA-B (see Chap. 15). These PSM-xxx codes have disappeared from IHEP catalog. The maximum dimensions of the bulk scintillators are $200 \times 50 \times 10$ cm, with a production of up to 100 tons per

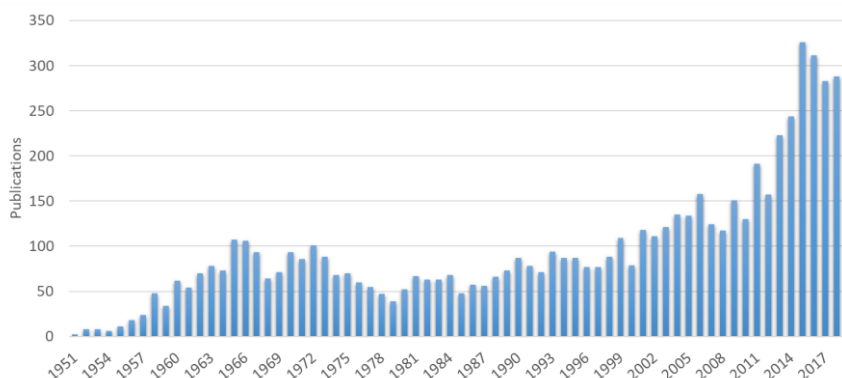


Fig. 1.2 Number of publications referring chemical modifications of plastic scintillators and sorted yearly (source: SciFinder[®], as of November 2019)



Fig. 1.3 Catalog front covers of Nuclear Enterprises (1980), Bicon (1990) and TESLA (late 1970s), and advertisement of National Radiac INC. (this advertisement is reproduced from [22] with permission from the American Chemical Society)

year. Reference [24] presents all the key developments of IHEP in the field. In Ukraine, the *Institute of Scintillating Materials* (ISMA) was established in 2002 as a part of *Institute for Single Crystals* who found birth as early as 1955. ISMA has extended its inorganic research expertise to several other materials, including thus

plastic scintillators. Former Czechoslovakia also has a long history in scintillators, whose research and development work started as early as 1952 in the Research Institute of Electronic Physics. In 1959, research and production were associated to the *TESLA National Corporation*. In early 1990s, part of this institute was transformed into a private-owned company called *SM&D (Scintillation Materials and Detectors)*. This company was then acquired by *Envinet a.s.* in 2008, then *Nuvia CZ* in 2016.

In 1990, *Bicron* claimed a production capacity of 12 tons of plastic scintillator per month. It seems that *Saint-Gobain Crystals and Detectors* acquired both *Nuclear Enterprises* after 1987 and *Bicron* after April 1993. In 1997, *Eljen Technology*, a subsidiary of *Ludlum Measurements* was created by C. Hurlbut (formerly from *Bicron*) in Texas.

It is also worth mentioning *Kuraray* from Japan, who started the production of scintillating fibers but also some plastics as early as 1982. In 2013, the discovery of the Higgs Boson was achieved in part with the use of these scintillating fibers. Currently, *Kuraray* is a global leader together with *Saint-Gobain Crystals and Detectors* in fibers technology. Table 1.1 inventories current manufacturers as well as some trade characteristics. It seems also that other companies may provide scintillators on-demand, such as *FUJITOK* [25] or *Plaken co., Ltd* [26] in Japan; such companies are not listed in Table 1.1.

Through history, it may be difficult to find reliable data on all commercial scintillators. Table 1.2 lists the various scintillator codes to their main property. This Table could be useful for further cross-comparison since several materials are now out of commercialization. Some other commercial PSs might incidentally be omitted. Despite this large choice (especially in the case of standard formulation, which are obviously both the most available and the most sold as well), there are still exciting chemical challenges to overcome and new possibilities to be discovered. They will now be described.

1.2 Plastic Scintillator Chemists

Figure 1.4 tries to overview the main teams, laboratories, institutes or companies that are currently or were previously involved in plastic scintillators modification, as well as their period of activity when the information is available. It may be sometimes difficult to judge whether some research is still active in some groups. Only the key-laboratories (with two or more publications written in this field) are shown, and collaborations cannot be added, so the publications are granted to the corresponding author.

Table 1.1 Main providers of plastic scintillators (in alphabetic order). Some companies may be resellers of other manufacturers

Name	Country	Trade codes	Estimated number of products
<u>Advatech UK Limited</u>	UK	n.d.	Amcryst reseller
<u>Amcryst</u>	Ukraine	UPS-xxx	> 10
Beijing Nuclear Instrument Factory	China	ST-4xx	n.d.
<u>Detec-Europe</u>	France	n.d.	Amcryst reseller
<u>Eljen Technology</u>	USA	EJ-2xx	21
<u>Epic-Crystal</u>	China	n.d.	1
<u>Institute for High-Energy Physics</u>	Russia	SC-2xx (bulk) SC-3xx (molded)	24
<u>Kuraray</u>	Japan	SCSN-xx	3
<u>Nuvia CZ</u>	Czech Republic	NuDET Plastic	2
<u>Perkin-Elmer</u>	UK	Meltilex®	1
<u>Rexon</u>	USA	RP-xxx	3
<u>Saint-Gobain Crystals and Detectors</u>	USA	BC-4xx	21
<u>Shandong Haiqiang Environmental Protection Technology Co., Ltd.</u>	China	n.d.	n.d.
<u>Win-Trust</u>	China	SPxxx	3

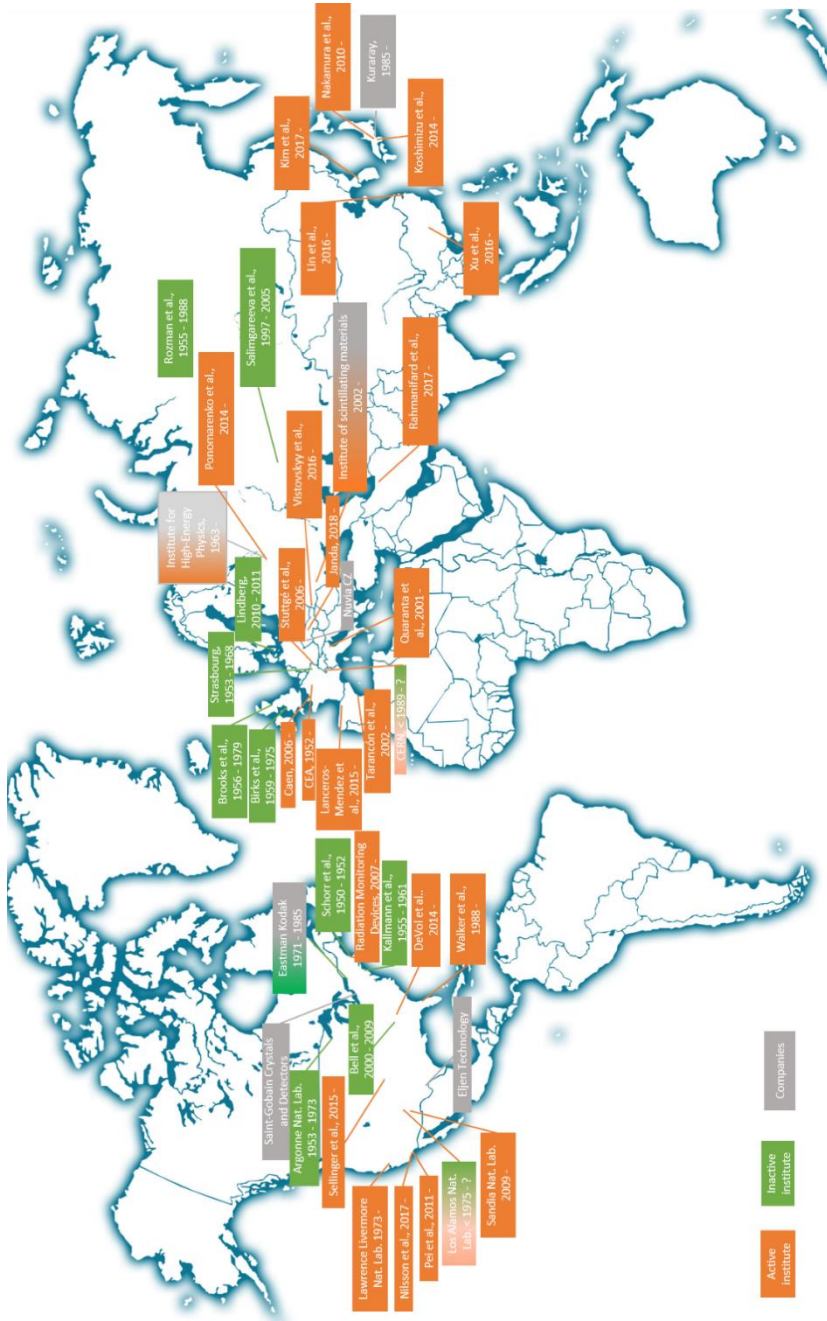
n.d. not determined

Table 1.2 Classification of past and current commercial scintillators. Scintillating fibers and prototypes are omitted

Main application	Scintillator code (alphabetical order)
General purpose	BC-400, BC-404, BC-408, BC-412, BC-416, EJ-200, EJ-204, EJ-208, EJ-212, NE 102A, NE 110, NE 114, Pilot F, RP-200, RP-400, RP-408, SC-201, SC-202, SC-205, SC-301, SC-302, SC-304, SC-306, SC-307, SC-308, SC-309, SCSN-38, SCSN-61, SCSN-81, SP32, SP101, ST-401, UPS-89, UPS-90, UPS-96, UPS-923A
Long decay time	BC-444(G), EJ-240, NE 115, UPS-92S
Ultrafast timing	BC-418, BC-420, BC-422(Q), EJ-228, EJ-230, EJ-232(Q), KL 236, Naton 136, NE 104, NE 104B, NE 111A(ZIP), Pilot B, Pilot M, Pilot U, Pilot U2, SC-206, SC-207, SC-305, UPS-91F
Green emitting	BC-428, EJ-260, EJ-262, SC-203, SC-204, SC-303, SP33, UPS-974
Red emitting	BC-430, NE 108*
Lead loading	BC-452, EJ-256, NE 142, SC-223, SC-322
Tin loading	NE 140, SC-221, SC-222, SC-321
Fast neutron/gamma discrimination	EJ-276(G), NE 150, UPS-113NG
Deuterated polymer	BC-436, NE 125
Boron loading	BC-454, EJ-254, SC-231, SC-331
High temperature applications	BC-434, BC-438, BC-440(M), BC-448(M), EJ-244, EJ-248, NE 160
Low energy gamma rays or X-rays	BC-450, NE 105
Radiation hard	PSM-115, SCSN-81T, UPS-92RH, UPS-98RH

* in Nuclear Enterprises catalog this scintillator is mentioned to emit at $\lambda_{\max} = 538$ nm, despite being classified as “red” plastic. However and according to the CIE rules, 538 nm is “yellowish green”

Fig. 1.4 Time and spatial repartition of laboratories and companies engaged in plastic scintillator modifications. Orange color is for active institutes, green for



1.3 The Scintillation Process in Plastics and Inorganic Materials/Crystals

Whatever the liquid or plastic nature, an organic scintillator can be resumed as a matrix that contains one or several organic fluorophores and potentially some loading for giving special application features. These fluorophores are usually called primary and secondary fluorophores, this name contracting to their respective role within the organic scintillator. In standard liquids or plastics, the matrix accounts for $\geq 95\%$ of the material, so radiation/matter interactions occur here. What happens after has been extensively described elsewhere [21] and will be introduced in several chapters of this book. In a few words, excitons are created and are transferred from the matrix to the primary fluorophore, usually (but not exclusively) by Förster Resonance Energy Transfer (FRET), which is a non-radiative transfer. The second process is radiative and undergoes emission/absorption between a donor and an acceptor; this is the roles of the primary and the secondary fluorophores, respectively. Ultimately, the emission wavelength and potentially the scintillation decay time are usually governed by the secondary fluorophores. But various exceptions exist.

Similarly, an inorganic scintillator can be seen as a host containing emitting centers. The later can be a doping ion or a point defect (extrinsic), but can be as well an intrinsic emitting species such as an exciton. At each level, chemical developments are still under review (e.g. quantum dots, conducting polymers, new loadings, crystal growth, etc.), but one has to admit that the “old” formulations are still particularly efficient and notorious. In the case of plastic scintillators, new formulations have been reviewed from time to time [27-32] and was discussed as well in several books [21, 33, 34]. The case of inorganic scintillators is rather different since they became highly specialized regarding the field of application (γ -ray spectroscopy, fast timing...) [35]. Given the large number of suitable polymers and fluorophores for scintillation as well as their respective concentration within the polymer, numerous formulations are possible, but the chemist has to respect the following fulfillments:

- The light yield, which is the number of photons emitted after radiation/matter interaction per unit of deposited energy, must be as high as possible and linear with the broadest absorbed energy range.
- Chemical loading gives special properties to the plastic scintillator but must not interfere (or at least to the lowest extent) with its light yield. In addition, it must result in chemically and environmentally stable material since plastic are usually used for several years with expected retention of the global performances.
- The material must be highly transparent to its own light (no self-absorption, eventually Stokes shift²), otherwise it will not be possible to use it at large scale.

² The Stokes shift is the numeral difference between absorption and emission wavenumber maxima of the same electronic transition. It is calculated as $\Delta\nu = 1/\lambda_{abs}^{max} - 1/\lambda_{fluo}^{max}$ in cm^{-1} .

- Depending on the application, a fast response might be required.

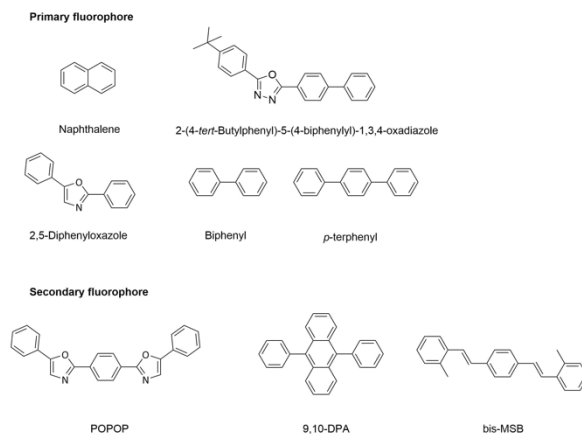
All these parameters will be fully described in this book.

1.4 Typical Preparation Process and Size Possibilities

Since plastic and inorganic scintillators differ from their chemical nature, their preparation process is extremely different.

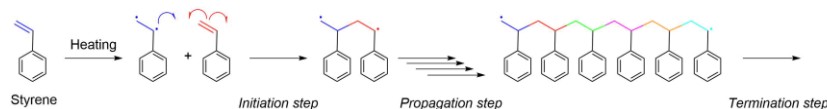
All the plastics that are available from commercial suppliers are prepared in the same way, which is the thermally-initiated radical polymerization. Two different aromatic polymers are usual: either poly(vinyltoluene) or polystyrene. Whereas the former is currently being used by major companies such as *Eljen Technology* or *Saint-Gobain Crystals and Detectors*, the latter is the choice of *IHEP*, *Nuvia CZ* and *Amcrys*. Thus, purified monomers are mixed with fluorophores and heated so that complete polymerization is reached. Heating breaks the styrene double-bond into two radicals, each of them being able to propagate with other styrene molecules, then creating oligomers and polymers. Scheme 1.1 represents a vulgarized polymerization of styrene, this reaction being valid for vinyltoluene as well as all other monomers that are able to polymerize under radical polymerization method. Bulk, classical polymerization conditions (100-150 °C for several days) lead to polymers with high molecular weight, more than 200,000 [36], and typically 230,000-500,000 g.mol⁻¹ [37]. Polymers with molecular weights higher than 50,000 have shown to display better light output than scintillators composed of polymers with shorter chains [38]. The correlation between residual styrene and quality of the transmission spectrum at low wavelengths has been experimentally determined [39]. For polymers of molecular weight 50,000, almost 10 % of styrene remains, and only 1.4 % of styrene is still present in the bulk monolith for molecular weight of 210,000 g.mol⁻¹. Also, residual monomer is pointed as a key cause for scintillator ageing. Other production methods than casting are possible: injection molding or extrusion. Here the quantity of residual monomer is very low but these two methods usually lead to lower-performance scintillator in terms of light output [40]. On the margin, 3D-printing and digital light processing emerged as a new production possibility but they usually show moderate performances against the standard preparation methods [41-48], but the extensive R&D currently performing in this area should benefit to the scintillation field in the near future. As an example, CERN has recently communicated on a proof of concept of a 3D-printed “super-cube” (two million cubic scintillators intended to be prepared with this technology) for neutrino oscillation experiments [49].

Fig. 1.5 Classical primary and secondary fluorophores used in most plastic (and liquid) scintillators



Since the polymer accounts for 70-97 % of the composition of the scintillator, most of the energy released by the impinging ionizing radiation is deposited here. One can understand that the polymer must present fluorescent and scintillating properties. As itself, polystyrene (and poly(vinyltoluene) as well) is a primary scintillator, but due to its high self-absorption at its own emission wavelength (300-350 nm), it is not possible to use it as such [30]. Adding a primary fluorophore to the polymer constitutes the first step towards efficient plastics, but still the attenuation length is below 10 cm. Finally, a secondary fluorophore, usually called wavelength-shifter, is added to the composition leading acceptable attenuation length (typically more than 1 meter) and a standard composition of plastic scintillator is found. Figure 1.5 shows classical molecules that act as primary or secondary fluorophores. Probably the most known primary fluorophores are 2,5-diphenyloxazole and *p*-terphenyl and they can be coupled to 9,10-diphenylanthracene (9,10-DPA), 1,4-bis(2-methylstyryl)benzene (bis-MSB) or 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP). Nevertheless, this list is obviously not closed and every year new molecules or luminescent systems are being evaluated. A noticeable limitation of the design of new plastic scintillators is their iterative process: preparation of various formulations, characterization and ranking according to their performances [31]. This methodology might be time-consuming and costly.

With such procedure, high quality and homogeneous scintillators can be produced with very large sizes as leading suppliers can prepare kg-scale slabs or cylinders. For example, *Saint-Gobain Crystals and Detectors* is able to provide 48 liters plastics with dimensions $6 \times 40 \times 200 \text{ cm}^3$ [50], and *Nuvia CZ* mentions the possibility to prepare up to 60 kg of monolith [51]. In fact, the volume of the final scin-



Scheme 1.1 Polymerization steps to polystyrene: initiation, propagation and termination

tillator is limited by the size of the oven used for heating the material while polymerizing. However, light scattering, heterogeneities of light production and collection may affect both light yield and energy resolution³ of the scintillator at such volume.

Inorganic scintillators can be prepared and used in various forms: single crystals, fibers, powders, thin films, aerogels [52], nanocrystals [35] and even hybrids [53], but the description of all the synthesis methods is out of the scope of this chapter. Note nevertheless, that the main difference is the melting point, as illustrated for typical inorganic scintillator (661 °C for NaI and 2050 °C for $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ (LSO)) rendering the cost productions for equivalent volume significantly higher.

1.5 Main Parameters and Tools for Modification or Improvement

Neither plastic nor inorganic scintillators can be considered as the “Holy Grail” in terms of radiation detection, so as the ultimate detector does not exist, and a careful choice must be performed when choosing the appropriate detector for the given application. Nonetheless, PSs can cover a broad range of applications, and above all their price compared with inorganic-based detectors can be a strong, even a decisive advantage. For example, PVT- and NaI:Tl-based detectors were compared for vehicle portal monitors applications [54]. Here, the balance is in the favor to plastic scintillator due to large number of traffic lanes that exist at border crossings and need to be equipped with such portal monitors, but the Authors conclude as “neither PVT nor NaI:Tl is a clear “winner” for all portal monitor applications [55].” Overall, the comparison might be tricky to realize since the two scintillators do not compete on the same performance skills and costs (as we will see thereafter).

So, if looking at pros and cons of using plastics versus inorganics, the main parameters are summarized in Table 1.3. It is somehow difficult to reference in an exhaustive way all the parameters that are useful for a radiological sensor, especially due to the versatility and the extreme diversity of both inorganic and plastic scintillators. Table 1.3 tries to reference the main parameters and the behavior of the materials under various external conditions. Here the cost of the scintillator (purchase from a supplier or laboratory production) has not been considered since it is not possible to make a comparison between all scintillators; so only material-related properties are discussed. For the inorganic world of scintillators, a very useful website has been created by Lawrence Berkeley National Laboratory [56]. As of No-

³ The energy resolution is defined as the full width at half maximum (FWHM) of the full energy peak at a given energy.

vember 2019, it was kept updated with numerous formulations, their main characteristics with suitable references. This is one of the most comprehensive database freely available for scientists.

1.5.1 Light Yield

When compared to the best inorganics, the light yield may represent one of the main limitations for plastics, and the key to success for better formulations (low density is another limitation, in particular for gamma spectroscopy). It seems that there is an upper limit of 10,000 emitted photons per deposited MeV by the impinging ionizing radiation for regular formulations. Going beyond this limit has been the subject of numerous research projects, since this parameter has a strong impact on the others: energy resolution of the scintillator, sensibility to low incident energies, quality of the pulse shape discrimination. For example, it is difficult to reference how many organic fluorophores were tested to improve the light yield, some of them being chemically speaking highly designed to this field [57-60]. An extension of this work has led some teams to (re)consider unitary scintillators, that is to say composed of only one molecule. Thus, *N*-(2-ethylhexylcarbazole) is a carbazole derivative that affords a liquid scintillator with an intrinsic light output of 6,000 ph/MeV [61, 62]. A 90:10 mixture of two silanes: (bis(9,9-dimethyl-9*H*-fluoren-2-yl)bis(phenyl)silane and tris(9,9-dimethyl-9*H*-fluoren-2-yl)(phenyl)silane can form an organic glass with a light yield that is superior to standard plastic scintillators [63, 64 and Chap. 8].

Various factors can affect the light yield: purity of the starting chemicals, choice of the chemicals (monomers – polymers, fluorophores, the latter being either organic or organometallic), preparation process (e.g. polymerization method), optical

Table 1.3 Main parameters for plastic and inorganic scintillators

Property	Plastics	Inorganics
Light yield	Up to 10,000 ph/MeV	Up to 100,000 ph/MeV
Decay time	0.3-280 ns, low afterglow	Down to sub ns
Emission wavelength	380-580 nm	180 nm-IR
Material loading	Multiple elements	Multiple elements
Effective atomic number	Low (mostly H, C and O): 5.7	Can be high (> 60)
Density	1.04-1.56	Up to 9
Radiation hardness	Up to \approx 30 kGy with γ -rays	Depends on impurities
Temperature dependence	Low below 40 °C	Can depend from low to high temperature
Humidity	Partially fogging with moisture	Some are hygroscopic
Magnetic field influence	Light output increase with magnetic field	No studies

improvements, etc. Standard fluorophores display excellent photophysical properties, with optically-excited quantum yield close to unity, which is not the case for PS or PVT. Since the polymer accounts for the main part of the scintillator formulation, various polymers with potentially better fluorescence quantum yields or properties have been tested: poly(methyl methacrylate) (PMMA) [65], poly(lactic acid) [66], poly(2-vinylnaphthalene) [67], polyimides [68-71], poly(ethylene naphthalate) (PEN) [72, 73], poly(ethylene terephthalate) (PET) [73, 74], poly(vinyl alcohol) (PVA) [75], (Styrene Ethylene/Butadiene Styrene) copolymer (SEBS) [76], poly(9-vinylcarbazole) (PVK) and carbazole derivatives [77, 78], polysiloxanes [79, 80], polycarbonate [81] and poly(phenyl sulfone) [82]. Except that for PVK, improving the light yield with other polymers was unsuccessful. Reference [32] gives more details on these possible polymer modifications, and a focus on polysiloxanes and their applications is available in Chap. 5.

Only a few materials were announced to overcome this 10,000 ph/MeV limitation, but all the reported high light yields were given in a relative way, that is to say against a commercial scintillator. All these materials contained organometallic compounds as the photoluminescent probe, with reported light yields of up to 32,000 ph/MeV, so three times the light output of a standard PS.

In addition, optical parameters have a strong influence on the final response of the scintillator: material self-absorption (especially in the case of pulse shape discriminating plastics) [83], global shape [84], nature of the covering layer (if any) [85], photon extraction [86], polishing quality of the surfaces [86], optical interface between the scintillator and the photosensor, surface covered by the photosensor [50], etc. One can see the important contribution performed in this field by the SuperNEMO experiment [86]. These optical questions are somehow the same whatever the nature of the scintillator. Several sections of this book will discuss about chemical or optical light yield improvements of the light yield.

As described above, the ideal and universal scintillator does not exist. A trade-off between global performances has always to be found in order to fit the requirements of the targeted uses. Some applications require the highest light yield. In priority, when high spectral resolution is required as for homeland security, the number of detected photons per interaction i.e. the statistics has a large influence, and halides doped with Eu^{2+} have been developed accordingly. Several compositions with scintillation yield approaching the theoretical limit have been discovered. Several low-band gap materials are now approaching the 100,000 ph/MeV [87]. These compounds exhibit these properties in the labs but production at large scale is not yet achieved. Among them, $\text{SrI}_2:\text{Eu}^{2+}$ is probably the most advanced [35]. Noteworthy are also the recent advances of co-doping $\text{NaI}:\text{Tl}$ leading to an energy resolution below 5 % [88]. In addition, non-proportionality also plays a major role, and the highest yield does not always show the best energy resolution. Various factors may affect the yield. In the crude model, the scintillation mechanisms are split in three stages: multiplication, transfer and luminescence, each step has to be efficient. The luminescence yield has to be almost 100 % and this is the reason why Ce^{3+} and Eu^{2+} are widely used. They combine a very high luminescence yield approaching unity and a rather fast recombination time. Eu^{3+} and Tb^{3+} are also efficient but show a

weak recombination rate leading to millisecond-range decay time. They are used as phosphors but not as single crystals. The multiplication stage is mostly driven by the forbidden band gap. Roughly, a small gap is generally preferred to favor the high number of secondary excitations. Regarding the transport stage, defects can be detrimental. A large interplay with the traps occurs in this stage and can lead to strong decrease of the scintillation yield and afterglow.

Noteworthy is the possibility to improve the external light yield of inorganics and plastics by imprinting the surface with photonic crystals. Chapter 9 will extensively present this breakthrough for plastics; ref. [89] is the most suitable for inorganics.

1.5.2 Decay Time

1.5.2.1 Main Component

Organic scintillators are known to be fast radiation detectors. In a perfect model the decay constant can be described as a monoexponential decay: $i(t) \propto e^{-t/\tau}$, with τ being the luminescence decay. However, most of the experimental decays are usually better described as bi-exponential (τ_{fast} and τ_{slow}) or even non-exponential decays. Most of the known PS decays fall within a range starting around a few hundreds of picoseconds up to almost 300 ns, with the whole range of decay times being covered. Ultrafast plastics are usually intended for use in ultrafast timing and counting [90, 91]. In the past, NE 111 and Naton 136 were very famous fast plastics. These materials are usually prepared from oxadiazoles such as PBD or butyl-PBD as the primary fluorophore (sometimes without wavelength shifter, limiting therefore their use to cm^3 volume only due to strong self-absorption process), and quenching of the photoluminescence can be performed with internal quenchers such as benzophenone, piperidine or other amines [92]. Such intermolecular quenching with low molecular weight additives seems to degrade the stability, thus the response of the scintillators [91].

On the opposite side, moderately slow [93] or slow scintillators [94] may find applications in dE/dx applications such as telescopes and phoswiches [95, 96]. It is noteworthy that such multiple-layered scintillator may also combine plastics with inorganics [97]. Only a few publications show the development of long-lived photoluminescent scintillators, and only one refers the use of the phosphorescence of an organic molecule, namely erythrosin B with a lifetime of 0.64 ms [98], but the material suffered from stability. The second possibility is to benefit from the chemistry of organometallics, such as the ones based on iridium(III) [99-103] or europium(III) complexes [104-106]. For example, $\text{Ir}(\text{mppy})_3$ in PVT or PVK displays a relative light output of 32,000 ph/MeV with a decay time of about 850 ns [99]. Such

fluorophore choice has been driven by the spin-metal transition that allows harvesting triplet states, thus possibly performing fast neutron/gamma pulse shape discrimination thanks to triplet state deexcitations. It is therefore not the same decaying pathway than the primary fluorophore high-concentration strategy, which is usually used for fast neutron/gamma pulse shape discrimination [9]. Such organometallic fluorophores (and more generally organometallic loading) will be described in Chap. 4. It is amazing to see that the decay of plastic scintillators can extend on almost six decades (Table 1.4)!

In the case of inorganic scintillators, the primary decay is driven by the radiative rate of the emitting center. It can be accelerated when non-radiative processes occur, but it is detrimental to the light yield. Such situation is not really of interest for scintillation except when pile-up has to be avoided. Note that quite often, non-radiative processes are connected with thermal quenching rendering the decay time and the yield temperature-dependent. The range of decay time is rather wide. Fastest scintillators are cross-luminescent materials (such as BaF_2 , main decay time being around 0.8 ns in addition to a slow component of 630 ns) but they generally show a slow component and emit in the deep UV. Direct band gap semi-conductor can be very fast but they generally show a strong self-absorption. ZnO:Ga is, as an illustration very interesting composition with this respect, with a 0.8 ns decay for the purest material [107]. Nanocrystals of semi-conductors are also under deep investigation. They exhibit a very fast emission due to the confined excitonic recombination. Self-absorption is still an issue, but in the case of 2D materials the fast bi-exciton emission is red shifted, and first attempts to use them for fast timing application are emerging [53]. Most common crystals are doped with popular activators such as Ce^{3+} leading to decays in the range of tens of ns, in the microsecond range for Eu^{2+} and Tl^+ , and in the ms range for Eu^{3+} and Tb^{3+} . Note that depending on the crystal quality, some afterglow may appear.

1.5.2.2 Afterglow

Contrary to their liquid equivalents, plastic scintillators are not known to display light afterglow. The delayed fluorescence of EJ-200 plastic scintillator has been recently measured in a time window ranging from 1 up to 10 μs [108]. The scintillation decay was expressed under the form of three exponentials with the corresponding weights: 7.8 ns (95.8 %), 490 ns (2.2 %) and 2,370 ns (2.0 %). The exact description of the photon distribution with time is mandatory when plastics are used in experiments with high rates, i.e. when the afterglow may become an issue.

As explained above, afterglow occurs during the transport mechanism. It corresponds to traps acting as intermediate states for free carriers. The sequence of trapping and detrapping prior to the transfer towards the activator delays its emission. The detrapping probability depends on the trap depth, its frequency factor and on the temperature. It is rather impossible to give some typical values, even for a composition since it may vary from a producer to another. Because the afterglow is connected to a competition for the charge carriers to be captured by the activator or by the trap, co-doping is often used to mitigate that effect. Among all the existing commercial compositions, one of the lowest afterglow is observed for CdWO₄.

1.5.3 Emission Wavelength

Intrinsically both families of scintillators are able to emit light in the whole visible domain. In the case of plastics, adding suitable wavelength-shifters allow tuning the emission wavelength, typically with λ_{em}^{max} from 380 nm (polymer with primary fluorophore) up to ca. 640 nm, violanthrone being the last emitting species here [109] (Fig. 1.6).

The violet wavelength ($\lambda_{em}^{max} \approx 420 \text{ nm}$) is the most referenced since it is the predilection domain of standard photocathodes of photomultiplier tubes. Green-emitting scintillators appeared as a wavelength-optimized coupling for solid sensors such as photodiodes and CCDs, and also as radiation-hard scintillators. Red-emitting scintillators are privileged when Cherenkov residual background strongly interferes with the signal. This effect can become an issue in dosimetry (see Chap. 12) and in fusion experiments (e.g. Laser Mégajoule facility). Interestingly, Boldt and Tsipis used wavelength difference between two plastic scintillators in anticoincidence, with appropriate filters in front of the photomultiplier tubes [110]. When the

Table 1.4 Examples of decay time values in plastics from 0.5 ns up to 370,000 ns

Polymer ^a	Fluorophores ^a	Decay time (ns)	Light yield (ph/MeV)	Ref.
PVT	PBD (40 g/L) quenched by acetophenone (5 %)	0.5	≈ 900	[89]
PS	EHCz (1-40 wt%)	14.9–22.1	1,230-2,700	[77]
PS	Proprietary mixture of two primary fluorophores	2.5–90	Not given	[93]
PVT	Ir(ppy-F ₂) ₂ (F ₂ -pic) (0.2 %)	793	7,300	[100]
EpoTek	2-Naphthoic acid	110,000	Not given	[98]
PS	Eu(phen)(DBM) ₃ (2 %)	370,000	5,650 ^b	[104]

^a PVT: poly(vinyltoluene), PS: polystyrene, PBD: 2-([1-biphenyl]-4-yl)-5-phenyl-1,3,4-oxadiazole, EHCz: *N*-(2-ethylhexyl)carbazole, Ir(ppy-F₂)₂(F₂-pic): (3,5-difluoro-2-pyridinecarboxylato)bis[3,5-difluoro-2-(2-pyridinyl)phenyl]iridium (III), Eu(phen)(DBM)₃: tris(acetylacetonato)(1,10-phenanthroline)europium(III). wt% stands for weight percentage

^b under alpha irradiation

first scintillator emits at 460 nm (PS + *p*-T + TPB + POPOP), the second emits at higher energies: 400 nm (PS + *p*-T). The concept of Spectral-Shape Discrimination was proposed by Feng et al. for fast neutron/gamma discrimination [100]. When excited with 2 MeV protons or 20 keV electrons, a poly(9-vinylcarbazole) scintillator containing Ir(ppy)₂(acac) emits photons at 515 nm and around 420 nm, respectively.

As for the decay time, the wavelength of emission is driven by the activator in inorganic scintillators. It ranges from deep UV down to IR. Some of the activators such as Eu³⁺ (red), Tb³⁺ (green) are rather insensitive to the host, and some others are strongly affected by the crystal field. As an illustration, Ce³⁺ emits in the UV in fluorides while it emits in the red in iodides and sulfides. Some recent research studies with activated materials by both Eu²⁺ and Sm²⁺ show an efficient energy transfer from Eu²⁺ to Sm²⁺, the latter emitting about 840 nm. These compositions show very good performances for gamma-ray spectroscopy (light yield in the range of 50,000 ph/MeV, energy resolution approaching 3 % and a decay time of 2 μs) while emitting in the IR: the material is even visually black [111]!

1.5.4 Behavior Against External Environment

1.5.4.1 Radiation Hardness

Radiation hardness is not an issue for radioprotection or homeland security applications, but it turns to reality when used in large experiments where the fluence is very high such as in Large Hadron Collider at CERN. For example, some calorimeters are composed of alternated slices of plastic scintillators and depleted uranium (DU), and an accelerated loss of transmission was noticed due to the natural radioactivity of DU (see Chap. 15). In the world of plastic scintillators, rad-hard materials has become the specialty of Zorn et al. in the 90's [112-114] and more recently of the Institute for Scintillating Materials, and *Amcrys* offers a “rad-hard” commercial PS (see Table 1.2). A recent review has been published in this field in 2019 [115].

Three strategies arise: first is to replace polystyrene by polysiloxanes [116]. For example, *p*-terphenyl and bis-MSB were dissolved in HARDSLIL[®] (a polysiloxane) and were exposed to a 400 kGy proton radiation dose. The results showed a 7 % only loss of transmission at 400 nm. However, the transmission does not relate the full story of the scintillation. PET and PEN polymers were also irradiated up to 140 kGy by the same team [117, 118]. Second is the use of fluorophores with exceptional Stokes shift: PMP [119] (although it seems that the same group later on discarded its use for such application a few months later [120]), or 3-HF and fluorinated flavones derivatives [121-124]. After degradation due to radiations, the transmission is reduced but molecules with high Stokes shift seem less affected than

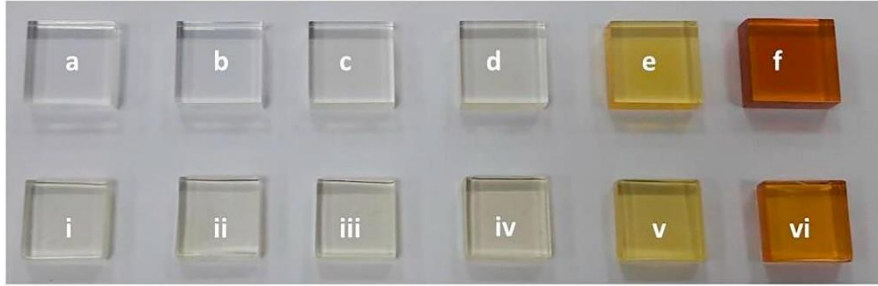


Fig. 1.7 Blue-emitting UPS-923A PS (top, a – f) and green emitting PS (bottom, i – vi) gradually neat, then exposed to 10^{13} , 10^{14} , 10^{15} , 10^{16} and 10^{17} n/cm² (reproduced from [126] with permission from Elsevier)

regular wavelength shifters. Third is the use of colored centers diluters. These “diffusion enhancers” are usually aromatic liquid molecules: 4-isopropylbiphenyl, 1-isopropyl- and 1-methylnaphthalene, *p*-xylene and 1,6-dimethylnaphthalene [122, 125]. In addition, the polymer is cross-linked so that it maintains good mechanical properties. Thus, a scintillator composed of 1.5 % of 4'-fluoro-3-hydroxyflavone, 8 % of 4,4'-divinylbiphenyl and 25 % of 4-isopropylbiphenyl as the diffusion enhancer presented an initial light output of 5,200 ph/MeV only but retained 94 % of this value when exposed to 33 kGy. However, their mechanical properties might be impacted by the addition of such high amount of liquid in the polymer.

Usually the radiation hardness is assessed under gamma exposition, but blue and green-emitting PSs have also been studied under a high neutron fluence ranging from 10^{13} to 10^{17} neutrons/cm² [126]. The visual aspect of these scintillators with the neutron dose is impressive with a strong amber-coloration due to the absorbed dose (Fig. 1.7). LEDs allow the scintillator to recover from radiation damage more rapidly [127].

Also of interest, fast neutron/gamma discriminating plastics were exposed to 10 kGy from a ⁶⁰Co source [128]. Several days after exposition, the scintillators were able to recover part of the light output as well as their yellow color vanished (Fig. 1.8). More surprisingly, the authors noticed that the quality of the neutron/gamma discrimination (the Figure of Merit value⁴) was improved after irradiation. ¹H NMR spectroscopy and High Resolution Mass Spectra Studies revealed the formation of a formic anhydride derivative of POPOP. This shows also that secondary fluorophores have also an impact on the n/γ discrimination performances (see Chap. 2). A similar study was also performed on EJ-299-33A prototype n/γ plastic [129]. After irradiation of 28 kGy, no n/γ discrimination remained visible. The influence of neutrons on the neutron/gamma discrimination performances of

⁴ The Figure of Merit value (*FoM*) is evaluated thanks to: $FoM = \frac{|\mu_n - \mu_\gamma|}{2.35(\sigma_n^2 + \sigma_\gamma^2)}$, where μ_n and μ_γ are the mean positions of the neutron and the gamma ray contributions, and σ_n and σ_γ are the standard deviations of neutron and gamma lobes. It determines numerically the quality of the neutron/γ discrimination at a given energy, usually expressed in keVee.

EJ-276 was also recently checked [130]. As expected, both light output and FoM value decrease with irradiation.

Regarding inorganic scintillators, the radiation hardness covers many aspects. The high energy colliders for high energy physics is for sure addressed in order to avoid the transmission losses induced, and the tremendous work regarding PbWO_4 in the frame of CMS benefited from the Crystal Clear collaboration [131]. The radiation hardness nevertheless covers several other aspects in many applications. As an illustration, thin films detectors for imaging or beam monitoring in the next generations of synchrotron facilities will receive significant doses to modify internal mechanisms. Beyond the transmission aspect, radiation induces defects may affect afterglow and internal yield as well. Even yield enhancement, called bright burn or hysteresis has been observed, such as in Eu^{2+} -doped BaAl_4O_7 scintillator [132]. This aspect is detrimental for medical imaging where the x-ray panel is not uniformly irradiated and a small local change of the yield is critical for the image quality. The same effect is really an issue in dosimetry that requires a very good linearity response with respect of the dose. As for the afterglow, traps are strongly involved in these “memory” mechanisms.

1.5.4.2 Temperature Dependence

Plastics are known to be robust detectors against temperature variations, especially in the range -20 - 20 °C. More than the scintillator itself, the {scintillator – optical transducer – photodetector} whole system has to be considered to temperature variations, with the photodetector being probably the most sensitive part of the system. In particular, scintillators for dosimetry may present exactly the same light output at room temperature (calibration) and at the temperature of the body (analysis, see Chap. 12). After the pioneering work of Rozman [133], Peralta studied the scintillation response of BC-404 PS and scintillating fibers in the range 0 - 40 °C [134]. BC-438 is a plastic scintillator that has been specifically designed for well logging

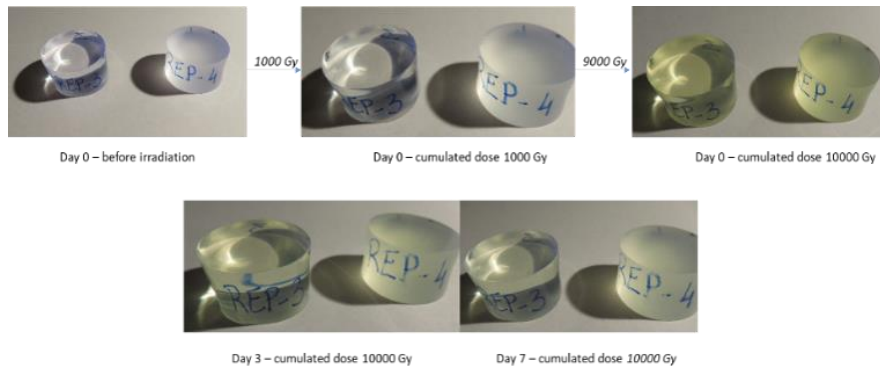


Fig. 1.8 Visual evolution of PSD plastics exposed to 10 kGy of gamma rays with time (reproduced from [128] with permission from the PCCP Owner Societies)

applications, where the temperature can sometimes reach 225 °C [135]. Its relative light output is 24 % of NaI:Tl, that is to say $\approx 9,000$ ph/MeV. When heating the material in a dedicated system (with a less optimized optical transducer), the light output goes from ≈ 14 % of NaI:Tl at 25 °C down to ≈ 4 % at 200 °C, with a reported light output variation slope of -0.02 %/°C in the range 25-50 °C. Unfortunately, the only information on this PS is its polystyrene base [136]; it means therefore that the scintillator is still usable way beyond its glass transition point (100 °C). BC-438 as well as BC-434 (another scintillator for high temperature experiments) are not anymore available in the *Saint-Gobain Crystals and Detectors* catalog. Cross-linked scintillators are copolymers that are prepared from styrene and another molecule bearing at least two polymerizable double-bonds, such as divinylbenzene or dimethacrylates. Such cross-linked polymers are already known from commercial suppliers (BC-440M, EJ-244) but recent publications have shown that the modified plastic scintillators had better mechanical properties [137, 138] and the light output was preserved when used at high temperatures, such as 120 °C [139], so higher than the T_g of PS or PVT.

Sometimes introducing new molecules to a topic may be followed by unexpected features. Sguerra et al. discovered that some of these complexes may be able to present thermoluminescent properties [103]. Thus, $\text{Ir}(\text{piq})_2(\text{acac})$ doped at 0.05 wt% in a plastic scintillator displays an intense thermoluminescence as a competitive process to scintillation and thus could be misclassified. Thus, charging this scintillator with ambient light at room temperature would lead to the release of the equivalent of 40,000 ph/MeV.

The main mechanism leading to thermal dependence of inorganic scintillator is the so-called thermal quenching, where the luminescent center shows a strong electron phonon coupling. This effect is not specific to scintillation and occurs under optical excitation as well. Famous scintillators such as PbWO_4 or BGO are fast because of the non-radiative recombination that operates even at room temperature. It affects thus the scintillation yield and the time response and in calorimetry where a stability of the scintillation response is required, the scintillator is thermalized. For oil logging and exploration where γ -spectroscopy is required, the temperature is largely increased at deep underground. At low temperature, afterglow often appears due to stabilization of trapped carriers and even a scintillation yield decrease can be observed. These aspects is of importance in the case of bolometry using scintillators. Another phenomenon is the decrease of the yield at large temperature due to phonon assisted auto-ionization as observed in YAG:Ce in the frame of LED application [140]. Finally, the scintillation response non-proportionality also depends on the temperature due to the dependence of the migration distances during the thermalization stage.

1.5.4.3 Moisture Effect

When mounted in radiation portal monitors, detectors are subjected to both temperature and humidity variations between night and day cycles. As a result, fogging

degradation can appear due to water permeation with the material, leading to unscheduled maintenance of the detectors. R&D teams from USA have extensively studied and proposed solutions to avoid this unwanted effect [141-147]. Around 200- μm micro-crazes appear throughout the whole volume, leading to useless detectors during months (Fig 1.9). This is usually the case for both PS- or PVT-based scintillators. More than the humidity itself, the combination with low and ambient temperatures might affect the material. Both internal (i.e. material modification) and external (coating) solutions exist to circumvent this effect.

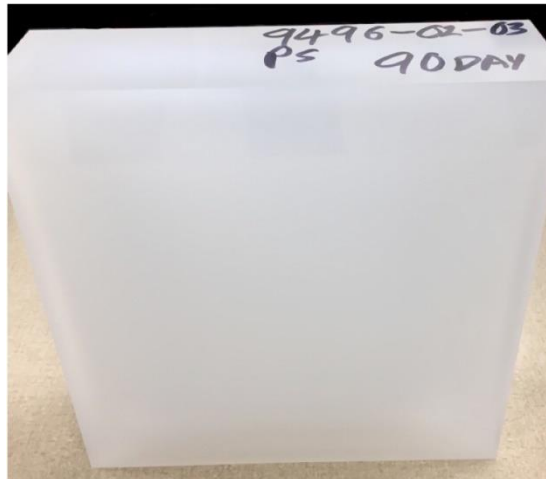
Sensitivity to moisture is the main chemical instability for inorganics, nevertheless, appropriate packaging are efficient. NaI:Tl and LaBr₃:Ce are illustrative hygroscopic but commercial products.

1.5.4.4 Magnetic Field Influence

At a glance, magnetic fields should be considered as having no or little influence on plastic scintillators' response. This effect is in turn of primary importance due to the strong magnetic induction taking place in colliders, calorimeters and magnetic resonance imagers.

Magnetic field dependence of the light output has been barely studied. In particular, the theory underneath this evolution is still unclear, without any supporting Monte-Carlo simulations. Rather than detector effects, the way the energy is deposited within the material could be modified with the magnetic field: exciton diffusion, changed Birks' saturation effect. Three major findings arise [148]: first, the light output increases with the surrounding magnetic field. Thus, up to 20 % more photons are created with magnetic fields up to 1.5 T. Most of this light increase is attributed to Cerenkov light production in the clear parts of the detector (e.g. optical fiber); when the signal is corrected, there is still an increase of 2.4 % of the light output [149]. Second, various formulations afford different patterns, as can be seen

Fig. 1.9 Example of temporary fogging of PS after hot and humid exposure and rapid cooling performed in a laboratory (reproduced from [145] with permission from Elsevier)



between SCSN-38, NE 102A and Polivar scintillators [150, 151]. The latter is a PMMA-based material containing 3-10 % of naphthalene and 1 % of butyl-PBD (and POPOP or BBD as wavelength-shifter) and shows the strongest field dependence. Despite their (small) polymer difference: PVT for NE 102A and PS for SCSN-38, both scintillators behave the same way between 0 and 0.45 T. Last, the results differ if the scintillator is a bulk monolith or a scintillating fiber. Chapter 12 will provide more insight of this effect on plastic scintillators and scintillating fibers.

The influence of magnetic field on inorganics seems poorly studied. At CERN/CMS, PbWO_4 has been installed in a high magnetic field calorimeter and seems safe for use.

1.5.5 Effective Atomic Number and Density

These parameters are essential to perform gamma spectrometry measurements, e.g. for the crucial application of homeland security, or when high-stopping power is required, and by essence inorganics are highly privileged against plastics. Since PSs are mainly composed of carbon and hydrogen, their effective atomic number Z_{eff} is around 5.7, so mainly Compton scattering occurs after gamma interaction with energies ≥ 100 keV. Here, organometallic chemistry and material engineering are powerful tools to add peculiar elements to plastic scintillators [152]. To increase Z_{eff} , heavy metals such as tin, lead or bismuth have been extensively studied [7], the main challenge being to load the material with large quantities of metal without affecting both optical transparency and light output. From these three metals, lead seems to quench the scintillation more than the two others do. Thanks to the use of tributyltin methacrylate as the organometallic (with 6 wt% of tin in the scintillator), a pseudo-gamma spectrometry is reachable at incident gamma energies up to the gamma emitted by ^{22}Na ($E_\gamma = 1,274$ keV) [153, 154]. This scintillator was reported to display around 6,600 ph/MeV under γ -rays excitation.

In fact, it is currently difficult to judge on a future substitution of inorganics by metal-loaded plastics. In some cases, the fraction of photopeak against all detected events seems too low to account for an acceptable, key-determining feature allowing determining the nature of the incident gamma ray. However, recent improvement in unfolding algorithms such as ML-EM (standing for Maximum-Likelihood fitting by Expectation Maximization method) appear extremely promising to resolve such spectra [155, 156]. Here as well, Chap. 4 on organometallic addition to scintillators will perform an in-depth understanding of this important loading, and Chap. 10 on new deconvolution algorithms will complete the discussion.

About the density, plastics are obviously driven by the matrix and heavy metal loading, even if high content does not change dramatically the metrics. Poly(pentafluorostyrene) affords scintillators with density 1.56, so 50 % higher than polystyrene or PVT [17].

Inorganic crystals are by far performing regarding the density and they are widely used for gamma-ray spectroscopy. The main effect of the density on the

scintillation yield, i.e. once the energy is deposited, appears on the so-called alpha/gamma quenching factor. The energy deposition of alpha particle in matter is driven by the Beth-Bloch formula. It means that the density of generated excitation is higher than under gamma ray excitation. It appears that high spatial density of excitation induces quenching, leading thus to a significant difference of scintillation yield between gamma ray excitation and alpha particle excitation. The ratio is called the quenching factor. Because dense material lead to higher density of excitation, they will be less favorable to alpha detection with this respect. As an illustration the quenching factor is 0.12 for LSO (d 7.4, Z_{eff} 66) and 0.15 for BGO (d 7.15, Z_{eff} 75.2) while it is 0.5 for NaI:Tl (d 3.67, Z_{eff} 50.8).

1.6 Summary

After 70 years of paramount discoveries, plastic scintillators cannot be avoided in various applications such as homeland security, nuclear batteries [157], environmental assays, radioprotection or personal dosimetry. In this chapter, we reviewed on a historical point of view the development of plastic scintillators, the key laboratories and companies and their main properties alongside with inorganics.

All the molecules that are involved in the preparation have been thoroughly investigated: polymer, primary fluorophore and wavelength-shifter. Still, there is a lot of room for improvement due to the large molecular and photophysical diversity. Loading the polymer with additives grants the scintillator with special features: gamma spectroscopy with organometallics, radiation hardness with diffusion enhancers, etc. The photophysical understanding of fast neutron/gamma discrimination is a stunning level. On this basis, it is not difficult to understand why these materials are so popular in the nuclear physics community. As a ultimate proof, the three new plastic scintillators – and probably others – that have been commercialized in the last ten years (EJ-276 from *Eljen Technology*, NuDET Plastic SP33 from *Nuvia CZ*, and UPS-113NG plastic from *Amcrys*) show that undoubtedly the research on new materials and/or new concepts is still challenging for cross-disciplinary teams of chemists and physicists. The chemistry of nanomaterials (e.g. quantum dots, metal organic frameworks, nanocomposites) has changed several paradigms and composites (mixtures of inorganic and organic materials) or hetero-structured scintillators combine the advantages of both families.

In addition to this chapter and the references herein cited, the Reader is encouraged to open the following reviews and book chapters that have been published after 2000. For plastic scintillators: reviews [8, 9, 31, 32, 65, 115, 158-167] and book or book chapters [7, 10, 157, 168, 169]. All these recent reviews undoubtedly demonstrate the high research activity in this field. For inorganics, please refer to these reviews [4, 35, 89, 160, 170], book or book chapters [171, 172]. For composite and hybrid materials please refer to [173-175] and Chap. 6.

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