

Review of Studies of Radiation Damage in Organic Scintillators

1 Introduction

Organic scintillators (such as toluene, polystyrene, and naphthalene) containing wavelength shifting additives in solution have long been popular elements in detectors used in particle physics, nuclear physics, radiation safety, and health physics applications due to their high light output, low cost, fast response, and versatility of physical construction. However, it has long been known that prolonged exposure of plastic scintillator to ionizing radiation has harmful effects: it can increase light self-absorption (yellowing) and decrease light yield. While much is understood as to the causes of this damage, much is still unknown. In this paper, first we give a brief summary of the physics of scintillation by organic molecules. Then we discuss what is known and not known about radiation damage in both solid and liquid organic scintillators.

2 Organic Scintillators

The scintillation mechanism for organic scintillators was studied intensively during the 1950s and 1960s, and is summarized in the famous book by J.B. Birks [1]. A useful review from 1993 for particle physicists can be found at [?]. Plastic scintillators and wavelength shifters, including wavelength shifting fibers, that are currently available from companies such as St. Gobain [2], Kuraray [3], and Eljen [4], are the direct descendants of those described in this work. The scintillation is due to the electronic structure of the carbon atoms in complex, organic molecules. Carbon has two 2S electrons. When forming compounds, one of these is promoted to a 2P state, where it can combine with hydrogen to form either saturated, double-bonded or triple-bonded hydrocarbons. In the most common scintillators, the 2S electron and the three 2P electrons combine to form a P state and 3 hybrid S-P states that are inclined at an angle of 120° (as seen in the hexagonal shape of polystyrene shown in Fig. 1 (a)). The electrons in the P state are called π electrons. The electrons in the hybrid states are known as σ electrons. The π electrons and their electronic states are the key to the most common kind of scintillation, such as that which occurs in benzene and polycyclic aromatic hydrocarbons (naphthalene, anthracene, naphthacene). The energy levels of the π electrons can be seen in the book by Birks [1], Fig. 3.7 or in Fig. 1 (b) (stolen from Wikipedia). The ground state is a singlet S state, with vibrational sub levels. There are also excited singlet states, each with vibrational sub levels, and a set of triplet states as well. In general, a charged particle transversing the scintillator excites the molecule from the lowest vibrational state of the 0S level to one of the higher singlet states. The excited molecule then decays down to the lowest 1S state. This lowest 1S state decays to one of the higher vibrational sub-levels of the 0S set of states, producing the fluorescence light, and then the molecule deexcites down to the lowest vibrational 0S state. Since the energy of the fluorescence photon is therefore smaller than the energy needed to excite the electron from this lowest state to any of the 1S states, the material is mostly transparent to this light, although there is generally a small overlap, at the lower end of the fluoresce spectrum, where absorption occurs. Since the vibrational sub levels of the ground and first excited singlet states are similar,

the absorption and emission spectra tend to be mirror images around the wavelength corresponding to the transition from the lowest 1S state to the highest 0S state (the emission photon energy is actually slightly smaller than the corresponding absorption energy at the minimum transition due to slightly different orbital configurations when the electron is in the 0 or 1 state[5].)

Modern plastic scintillators are not usually pure crystals, however. They usually contain a polymer substrate, such as toluene, polystyrene, or naphthalene, into which 2 types of organic scintillator “dopants” are dissolved. SCSN-38 has p-terphenyl and POPOP (2,2'-p-phenylene-bis(5-phenyloxazole).[?]. SCSN-81 probably has para-terphenyl (primary) and BBOT (secondary) [6]. Polystyrene and PVT are very common substrates. Polystyrene is a polymer made of repeating units (monomers), along a carbon main chain (backbone), as shown in Fig. 1 (a).

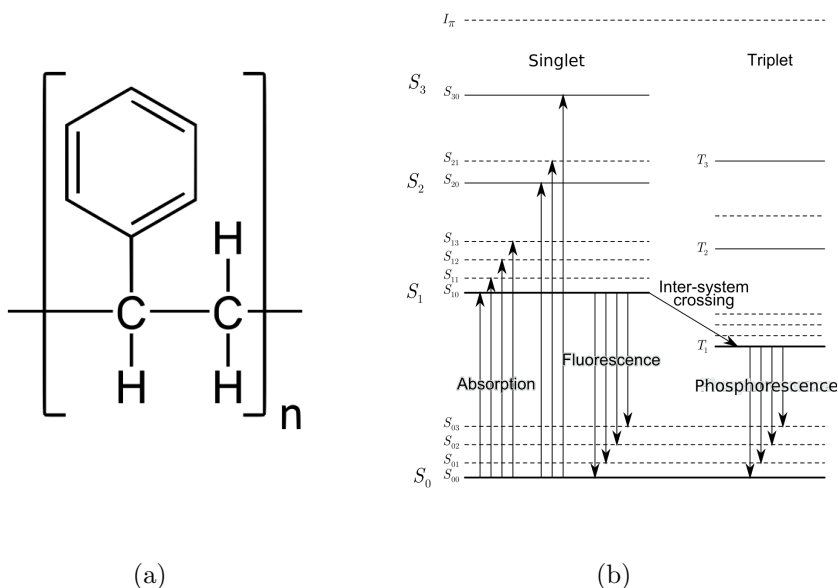


Figure 1: (a) Basic chemical unit for polystyrene (b) typical energy levels in organic scintillators (stolen from Wikipedia)

In this type of scintillator, as described in [1], a charged particle transversing the scintillator excites the substrate. The concentrations of the dopants are low enough that direct excitation is negligible. In general, either the π or σ singlet electrons of the substrate can be excited or ionized. Fast scintillation is generally related to the excitation of the singlet π electrons; the fraction of the energy loss of the charged particle via this mechanism, as opposed to the other possibilities such as excitation of the triplet states or ionization, determines the scintillation efficiency of the scintillator. Typically, this probability is two thirds of the fraction of electrons that are π electrons [1]. The excited singlet π electrons can then either de-excite through fluorescence (usually in the UV), non-radiative de-excitation (quenching, which can occur through internal collision, which is not affected by the molecule’s environment but is affected by its geometry which depends

on the polymer’s history, and via inter-system crossing, which is strongly affected by the environment and the geometry/folding of the molecule, as it needs magnetic perturbations to proceed [5]), radiative migration of the excitation to another molecule of the substrate, or non-radiative migration to another molecule. The radiative migration often involves UV light. For crystals, exciton (the excited state) diffusion is the most important mechanism for diffusion; for liquids, it is solvent-solvent resonance (transfer of the excitation via dipole-dipole interactions of two molecules) and thermal diffusion (collisions) [1]. Migration is important for common scintillators, as this can transfer the excitation of the substrate to the dopant, and thus lead to the emission of the detectable light. A second dopant is often added to shift the wave length of the light to one suitable for existing photo-detectors. We refer to these two types of dopants as the primary dopant and the wavelength-shifting dopant.

3 Radiation Damage in plastic scintillators

Radiation damage in scintillators was intensely studied during two periods: during the late 1950’s and early 1960’s, when scintillators were first being understood, and during the late 1980’s and early 1990’s, when detectors for experiments at HERA, the SSC, and the LHC were being designed.

Radiation damage was first observed by Birks and Black [7] in pure anthracene crystals. In [8], from 1957, Rosman and Zimmer studied polystyrene and polystyrene with different concentrations of paraterphenyl (PT) as primary dopant and 1,1,4,4-tetraphenylbuadiene (TPB) as either a primary dopant or used as a wave-length shifter for the PT. They found that the radiation-induced self absorption of light is stronger for shorter wavelengths. They also found that the number of induced color centers (which is the inverse of the absorption length) is linear in the dose. Both results have been confirmed by many studies for moderate doses (< 5 Mrad), at which point production of additional types of radicals opens up and concentration saturation of the benzyle radical occurs, resulting in an increase in the complexity of the damage [9].

While there were many studies of radiation damage by particle physicists during the late 80’s, the most scholarly (meaning educational for particle physicists who do not know much chemistry) are those of Klaus Wick and his diploma students at the University of Hamburg [10],[11],[12],[13],[14],[15] And by Bodman and Ulm, also from Hamburg [16],[17]. Bross and Pla-Dalmau [18] also contains much useful information, once you have learned enough chemistry to understand it. Unfortunately, some of these works have contradictory conclusions. Most of these studies, however, concern the induced decrease in absorption length, except for some very early studies at very high doses and dose rates, and an interesting discussion in [11], that we will discuss in detail later, on decrease in light output.

In order to understand radiation damage to organic scintillators, it is important to understand the basic chemistry involved. In [15], Wick *et al.* detail the chemistry of radiation damage in polymers. When an ionizing particle interacts with the polymer substrate, it can break the weak bonds the bind the oxygen, carbon, and hydrogen. Todd[19]

proposes that radiation first ruptures a C-H bond. This can lead to the production of radicals (such as $\cdot\text{CH}_3$, $\cdot\text{OCH}_3$, $\cdot\text{COOCH}_3$, where the \cdot stands for a single dangling bond) that absorb fluorescence light (color center) and lead to a permanent increase in light self absorption. They can affect the environment of the other molecules, leading to an increase of non-radiative decays. When these bonds are broken, gas creation (evolution), polymer degradation (breakage of the polymer main chain (backbone) to the original monomer), and polymer cross linking (when one or more polymer chains are joined by short, long, or even polymeric molecules, usually by removal of a hydrogen, although in polystyrene this also involves hydroperoxide groups due to removal of a water [19]) can also occur[11]. This again affects the local environment for the other molecules, and can change the energy levels for the broken strands, so that their radiative transitions are no longer of appropriate wave length. The change in energy levels can also enhance nonradiative decay modes. For polystyrene, radical production and cross linking are important [11]. For other substrates, different mechanisms can be dominant [11]. The result can be absorption of radiation, less radiation and less transfer of the excitation to the dopant.

Radicals can migrate through the substrate, although the mechanisms for this depend on whether or not oxygen is present. If oxygen is not present, migration occurs via hydrogen abstraction reactions. However, when oxygen is present, additional reaction channels open. Wick *et al.* list five additional migration mechanisms. Note that cross linking of polymers severely reduces their ability to migrate [20]. Since radicals can annihilate, migration can provide a mechanism for temporary light loss or temporary light self-absorption. Oxygen can change radicals from types that absorb in the UV and visible to peroxide radicals, which do not. It is thought that this is the mechanism through which “bleaching” of radiation damaged scintillator occurs, after (or even during) the exposure (where bleaching is a decrease in the radiation-induced self-absorption with time).

Since the effects depend in detail on the types and quantities of the various different damage possibilities (the radicals produced, the importance of cross-linking versus degradation, the mobility of the molecules), the detailed result on the optical qualities of the scintillator can vary. For example, the behavior of scintillators containing even small quantities of naphthalene in the presence of oxygen is completely different than those that do not, even when based on the same substrate[11]. Note also that some measurements [19] indicate that discoloration (radiation-induced absorption length) of polystyrene in vacuum is only due to radical production from manufacturing impurities, perhaps interacting with oxygen, and not due to radical production from the polystyrene itself. The manufacturing method for the substrate and temperature treatment during manufacturing can have a strong effect [21] [22], as this can effect polymerization, content of gases, the diffusion constant, and mobility of radicals. Heating of the plastic after irradiation is another way, beyond oxygen diffusion, to increase the mobility of the radicals and remove color centers. Polystyrene is especially sensitive to temperature treatment [21]. If exposed to temperatures above 70°C before or after irradiation, the damage is increased.

Wick *et al.* [11] have done many studies on the influence of the diffusion of oxygen on induced self absorption in materials like polystyrene and PMMA (polymethyl methacrylate). They show that the penetration depth of oxygen into the substrate depends on the

dose rate, presumably because interactions of the oxygen with radicals affects its ability to diffuse. At lower dose rates, oxygen penetrates more deeply. Because of the importance of the interaction of oxygen with radicals, this can lead to dose rate effects for radiation damage. They also show that the recovery of the induced self absorption after irradiation (bleaching) is consistent with oxygen diffusion. They show that there is little bleaching without oxygen, and that a very large number of color centers form if there is no oxygen, although the permanent damage after bleaching (exposure to oxygen after the radiation) is slightly larger if there is oxygen. A similar discussion exists in Bross and Pla-Dalmau [18]. They looked at dose rates of 1 Mrad/h and 0.03 Mrad/h for a total dose of 10 Mrad. They found no dose rate effect in inert atmospheres, confirming the role of oxygen for permanent induced absorption. They found more permanent damage if the samples were in a pressurized oxygen atmosphere (2 atm.), although they also comment that annealing (reduction of the non-permanent losses) is aided by oxygen. In general, oxygen during irradiation seems to increase the permanent damage, even after annealing. However, if there is no oxygen present, there is no annealing, and the induced self absorption can be very large. In [15], Wick develops a model that explains both the temporary light self absorption and its time dependence, and permanent induced self-absorption in terms of oxygen diffusion.

Studies on the effect of radiation on the light yield are fewer than those on self-absorption. In an early study, Rosman and Zimmer found, after correcting for any induced self-absorption, that the light output versus dose is described, approximately and for relatively large dose rates, by a double exponential, with a small-dose component whose constant is approximately 100 Mrad, a large dose even by modern standards. The exponential constant was smallest for pure polystyrene, while that of polystyrene doped with 1.5% PT and 0.02%TPB was slightly larger. The constant was considerably larger (less self-absorption of light) for 3% TPB. They also used UV light to illuminate the samples with 1.5% TPB, and found that this showed less reduction of light than excitation via charged particles. Since the polystyrene substrate is transparent to UV, this indicates that the TPB was not damaged, and instead the damage should be either to the polystyrene or the migration of the polystyrene to the dopant.

In [23], from 1958, Berلمان studied liquid scintillators that used xylene as the substrate and diphenyloxazole (PPO) as the dopant. He found that the decrease in light output with dose could be reduced with higher concentrations of dopant. He also found that if irradiated dopant is put into an unirradiated substrate, the light output is still good. His studies confirm that an important source of the reduction of light output is due to reduced migration from the substrate to the dopant or deexcitation of the substrate via heat. A 1992 study by Bross and Pla-Dalmau, using polystyrene, reached similar conclusions [18].

In [11], Wick also studies decreased light output for a plastic scintillator from Kuraray, SCSN-38, which is based on polystyrene with b-PBD and BDB dopants. The main absorption wavelengths for polystyrene typically range between 230 to 260 nm, for the primary dopant b-PBD between 270 to 330 nm, and for the wavelength shifting dopant BDB between 310 to 400 nm. They found that light loss was much stronger in the presence of oxygen. Note that while oxygen plays a beneficial role in regards to annealing of induced absorption length at the end of radiation, it plays a detrimental role

in regards to light output. They also found the light output loss was independent of the wavelength of the light that was used to excite the scintillator, when it was varied between 230 and 400 nm. From this they conclude that the damage is due to destruction of the second floor. This is different than what was found in earlier studies, which indicated that damage to the dopants was small and that damage was mostly to the substrate, although different dopants were used. By looking at the damage as a function of the thickness of the scintillator, they concluded that the BDB molecules are mainly destroyed near the surface, which lends support to a mechanism involving oxygen diffusion.

If the damage is due to oxygen diffusion, a dose rate effect is expected. An interesting new result is due to Biagtan *et al.* [24], in 1996. They look at light output reduction for two polystyrene-based scintillators (SCSN-38 and SCSN-81) and a polyvinyltoluene-based scintillator (Bicron-499-35). They find a reduction in light output that depends linearly on the log of the dose rate for dose rates ranging from 0.01 to 2 Mrad/hr. Note that the effect is not small: for a dose of 2 Mrad, the light loss is negligible for a dose rate of 2 Mrad/hr but 20% for a dose rate of 0.01 Mrad/hr for SCSN-81.

If this dose rate effect is due to oxygen diffusion, then we expect it to be governed by the diffusion equation. Since the oxygen diffusion depth is greater at lower dose rates, we expect the damage for the same dose at different dose rates to increase up to the point where the dose rate is low enough that oxygen permeates the entire sample. The dose rate effect should plateau at this point. Specifically, we predict that the light output reduction should depend on both the dose and the dose rate as:

$$L(R, D) = 1 - [f(D)Z(R) + a(D)(1 - Z(R))]$$

where L is the % light yield, D is the dose, R is the dose rate, $Z(R)$ is the fraction of the scintillator containing oxygen and is given by $\min(\frac{2z_0(R)}{d}, 1)$ where d is the thickness of the scintillator and z_0 gives the depth of scintillator penetrated by oxygen, $a(D)$ is related to the fraction of quenching in the part of the scintillator containing oxygen and is given by $1 - e^{-a_0 D}$, and $f(D)$ is related to the fraction of quenching in the part of the scintillator not containing oxygen and is given by $1 - e^{-f_0 D}$. The diffusion depth $z_0(R)$ is given by diffusion theory as

$$z_0(R) = \sqrt{\gamma/R}$$

where γ is a property of the substrate and the radicals that are dissolved in that substrate during the diffusion process. The value for γ depends on the material, oxygen pressure, radical concentration (which is proportional to the dose) and temperature. The minimization in $Z(R)$ occurs because the fraction of scintillator containing oxygen can not exceed one. Note that this equation assumes the temperature and the surrounding atmosphere is held constant, as this can affect diffusion.

Figure 2 shows a fit of our theory to the Biagtan data [24] for SCSN-81 and for B-499-35. The fit is not bad, with γ of 0.35 ± 0.007 , f_0 of 0.092 ± 0.005 , and a_0 of 0.029 ± 0.003 for SCSN-81. For B-499-35, the results are γ of 0.092 ± 0.012 , f_0 of 0.088 ± 0.004 , and a_0 of 0.006 ± 0.003 . The model clearly predicts a knee when the rate $R = \frac{4\gamma}{d^2}$. For the Biagtan data, this is at a dose rate of 10^{-2} Mrad/hr, which is slow for a reactor test but large for actual operating detectors. The data, unfortunately, does not extend below dose

rate of this value, except for the very largest doses. As explained in [9], the chemistry of radiation damage changes for doses around 5 Mrad. The model also predicts that the knee should occur at higher dose rates for thinner scintillator, but no data is available on this either.

Logically, also, the linear trend seen in the log of the dose rate must fail at very low dose rates, and some kind of knee must eventually occur. Unfortunately, real detectors operate at these very low dose rates, and there is no data or verified model to do the extrapolation.

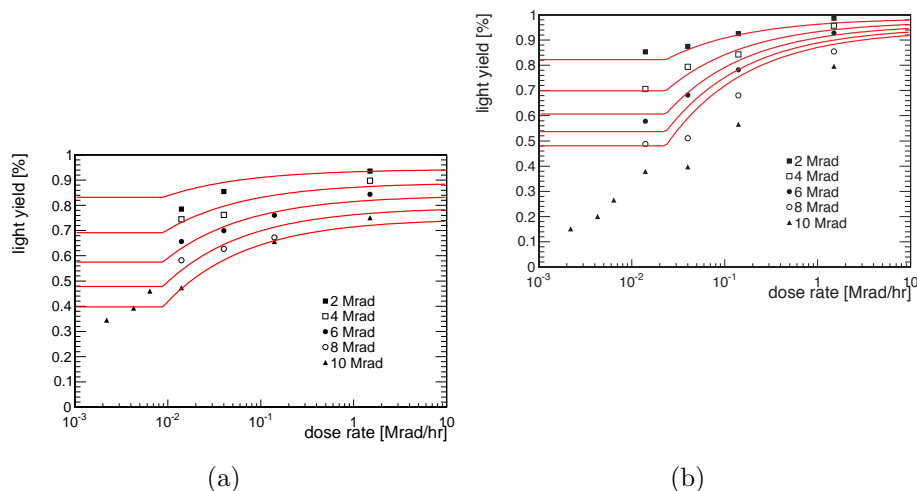


Figure 2: Fit of our model for the fractional light output relative to unirradiated scintillator as a function of both total dose and the dose rate to the Biagtan data [24] for SCSN-81, which uses polystyrene as its substrate (top) and B-499-35, which uses polyvinyltoluene (bottom).

While there are still mysteries on solid plastic scintillators fluorescing in the blue, very little published data is available on liquid scintillators and on scintillators operating at longer wave lengths than blue. A 1992 paper by Bross and Pla-Dalmau [18] shows that using a 3HF dopant does that scintillators operating at longer wave lengths are less affected by radiation damage. There is no information on dose-rate effects. The published works on liquid scintillators that we were able to find was by Zorn [25] in 1990, the paper discussed previously from Berلمان in 1958, and a paper by Klein from 1967[26]. There is also unpublished work from CDF using Bicron517L[27] and [28]. There is also an unrefereed difficult-to-obtain conference proceeding on pyrex tubes filled with liquids [29]. Neither measure the properties of modern liquid scintillators that are rumored to be radiation resistant.

4 Bibliography and References cited

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