

PROGRESS IN PLASTIC SCINTILLATORS

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There are three general classes of luminescent substances used as scintillation detectors; inorganic crystals, organic compounds, and inert gases. Plastic scintillators can be considered as solid solutions of luminescent organic compounds in a transparent plastic medium. Thus they can be classed as a special group among organic scintillators.

The development of plastic scintillators began in 1950 when Schorr and Torney (1) reported that solid solutions of p-terphenyl in polystyrene produced scintillations upon excitation with ionizing radiation. Since that time there has been a considerable accumulation of data on such categories as

- 1) recipes for producing plastic scintillators of various sizes and compositions,
- 2) luminescent properties of solutes in a plastic medium,
- 3) effects of the plastic medium on the mechanism of energy transfer in the scintillation process, and
- 4) the use of plastic scintillators to detect ionizing radiation.

1. PREPARATION OF PLASTIC SCINTILLATORS

The most common method of preparation of a plastic scintillator is by the thermal polymerization of a solution of the solute in the monomer. (2-5) Polymerization procedures vary with the composition

and size of the sample desired. For large samples, polymerization is initiated slowly at lower temperatures (90-100°C) and then completed at a higher temperature. (6, 7)

It has been found that a higher luminescent efficiency can be obtained if the monomer is purified to eliminate inhibitors. This is generally done by vacuum distillation of the monomer before use. The removal of oxygen before starting the polymerization will also produce a more efficient scintillator. The use of initiators such as benzoyl peroxide tends to reduce the luminescent efficiency. (8)

Other methods for the preparation of plastic scintillators include such techniques as molding a mixture of polymer with some solute, or casting ready made plastic scintillators. Plastic scintillators prepared by these methods are usually found to be slightly less efficient.

The most common monomers used to prepare plastic scintillators are styrene or vinyl toluene. In order to find a more efficient monomer, a systematic study of different monomers has been carried out. The results of the study will be presented in the following paper.

A large number of different organic luminescent materials have been tried out as solutes for preparing a more efficient plastic scintillator. (2-5, 8-9) Some solutes have been fairly successful, e. g., p-terphenyl, 2-phenyl-5-(4¹-biphenyl) -1, 3, 4 oxadiazole (PBD), 9, 10-diphenylanthracene, etc. Pichat and Koechlin (2) increased the luminescent efficiency by adding small amounts of 1, 1, 4, 4-tetra-phenylbutadiene as a secondary solute. Since this report, numerous combinations of primary and secondary solutes have been tried in order to produce a more efficient scintillator. Thus far the most efficient primary solute known to the author is PBD; the most efficient secondary

solute is p,p-diphenylstilbene. Typical results of light output vs concentration of solute are given in Fig. 1. The light output values are relative to a standard anthracene crystal. The best commercially prepared plastic known to the author contains a combination of p-terphenyl and p,p-diphenylstilbene.

In doing work with plastic scintillators, one must be extremely careful that the solutes are of very high purity. This can be easily checked by measuring the absorption and emission spectra of the solutes. Unfortunately some of the confusing data in the literature can be traced to using compounds of questionable purity.

Various attempts to increase the photosensitivity by incorporating heavy metals in plastic scintillators have had very limited success. (2, 5, 10) This is due to the large quenching action of the heavy metal. However, a plastic scintillator that Hyman (11) successfully loaded with 5% lead gave a pulse height equal to 70% of that of the unloaded plastic. This lead-loaded plastic did give a measurable photoelectric peak. Results are shown in Fig. 2.

2. LUMINESCENT PROPERTIES OF PLASTIC SCINTILLATORS

An excellent review of the luminescent properties of plastic scintillators has been written by Rozman and Kilin. (12) In the short time allowed, it is impossible to review all the work that has been turned out so only some arbitrarily selected topics will be discussed.

The luminescent yield of a plastic scintillator is temperature dependent for some solutes. Rozman (13) investigated this phenomenon

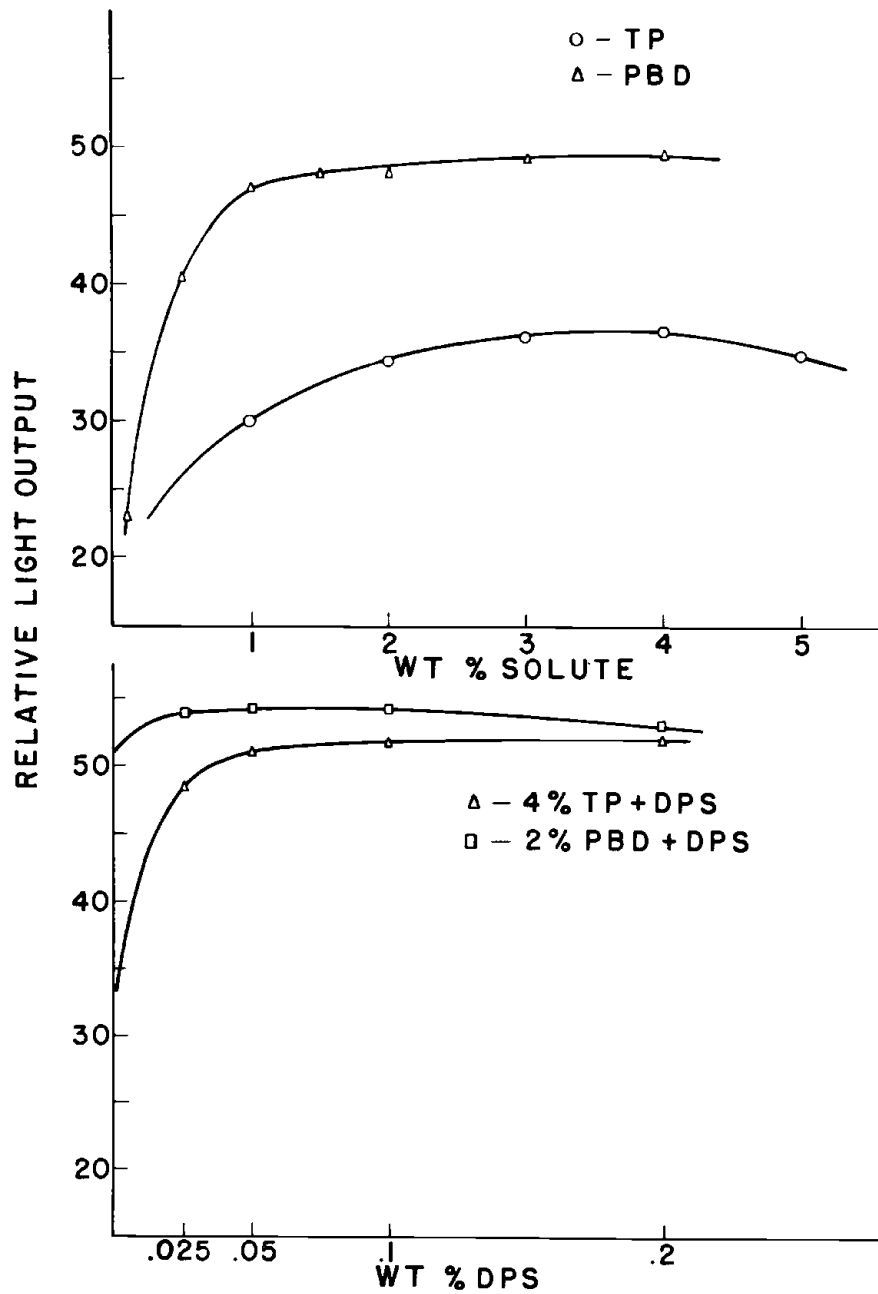


Fig. 1. Light output vs. concentration of solutes in polyvinyltoluene. Source: beta rays from Cs^{137} . All light output values are relative to a standard anthracene crystal. (Reprinted from reference 5 with the kind permission of the editor.)

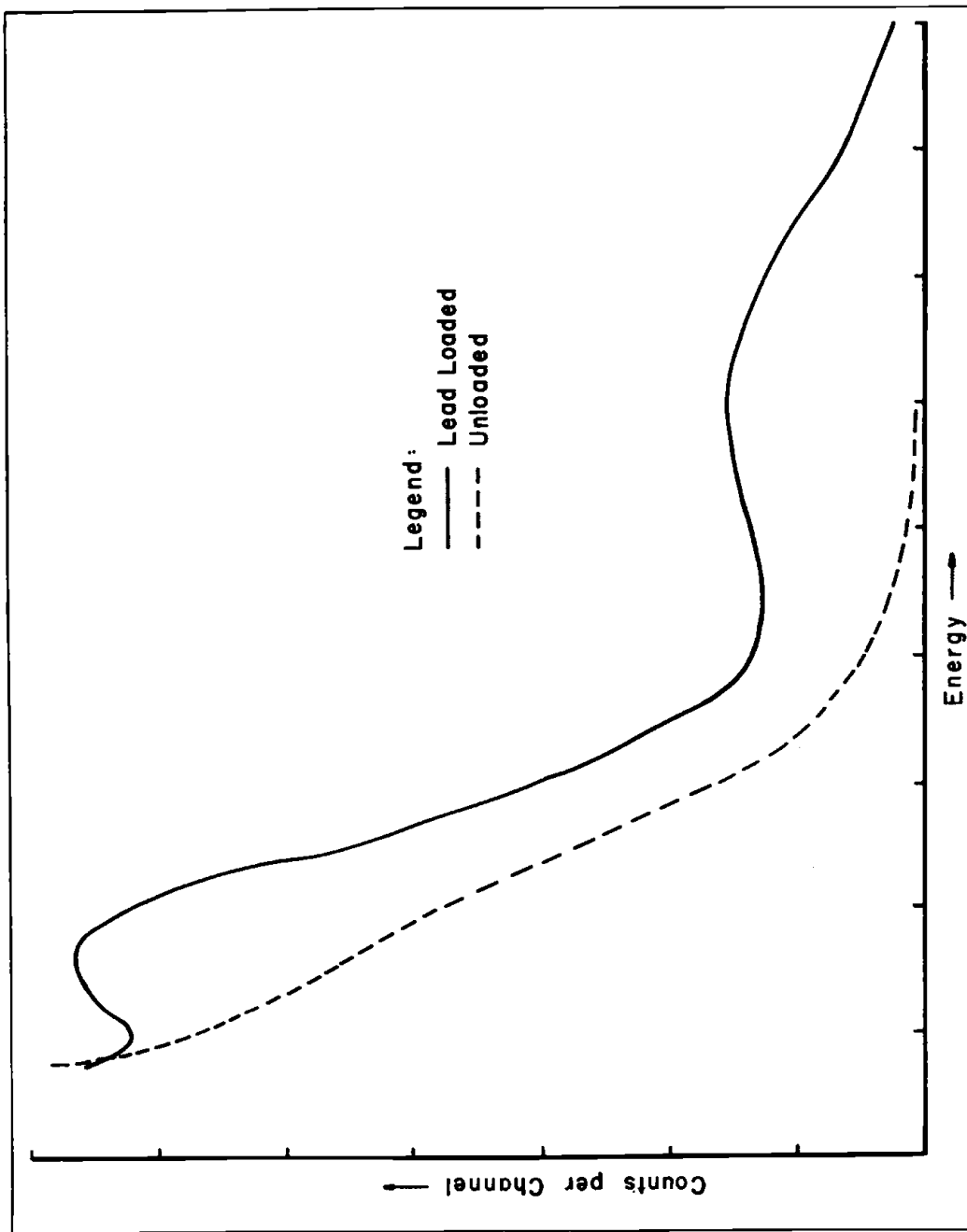


Fig. 2. Pulse height spectrum of lead-loaded plastic scintillator vs. unloaded plastic scintillator. Source: Co^{57} ; $E_\gamma = 123 \text{ kev}$. (Reprinted from reference 11 with the kind permission of M. Hymán.)

for several different solutes. For p-terphenyl in polystyrene the luminescent yield changed very little over a wide temperature range. For other solutes (e. g. , 1, 1, 4, 4-tetraphenylbutadiene) the temperature coefficient is larger and may even change sign.

The principal results of fluorescence studies on plastic scintillators are as follows. The emission spectrum observed for a plastic scintillator usually corresponds to the fluorescence spectrum of the solute added. In most cases the observed spectrum is the same for both plastic and liquid solutions. Exceptions to this are for anthracene and p-terphenyl in polystyrene. Several authors have shown that anthracene enters into a chemical bond (i. e. , copolymerizes) with styrene during polymerization. (14-16) It has been reported that the fluorescent spectra of concentrated solutions of p-terphenyl in polystyrene contain the bands of the crystal. (17) This suggests that p-terphenyl is imbedded in the plastic medium as microcrystals.

As expected, the fluorescent intensity increases with increasing solute concentration. Maximum intensity is usually reached at a solute concentration of 1 to 4%. In a system consisting of a primary plus a secondary solute, the emission spectrum corresponds almost entirely to the fluorescent spectrum of the secondary solute. The fluorescent spectrum is influenced by the reabsorption processes. The degree of reabsorption depends on the dimensions of the plastic scintillator.

3. USE OF PLASTIC SCINTILLATORS TO STUDY THE PROCESS OF ENERGY TRANSFER

In investigating the luminescent properties of plastic scintillators,

a question that arises immediately concerns the mechanism by which the relatively high energy of a charged particle is transferred to some fluorescent solute. It has been convenient to divide this over-all process into two separate categories. The first process includes the deceleration of the charged particle and transfer of its energy to molecules of the medium. The second phase includes all processes that occur until the activated molecules lose their excitation energy. Thus far, the larger amount of work in plastic scintillators has been centered around the second of these two categories so the first (and possibly more fundamental) is still very imperfectly understood.

There are several advantages, or disadvantages (depending on the particular viewpoint), to using the plastic medium for studying energy transfer processes. The most notable characteristic of a plastic is that the medium is rigid so that the Brownian motion of molecules and radicals is limited. Moreover, mechanisms involving collisions and diffusion of molecules can be excluded. One can also exclude such problems as oxygen quenching. However, there does appear to be some surface deterioration of plastics left standing in air. It is important to have a freshly cut surface on a plastic if meaningful measurements are to be made.

Using a plastic scintillator for studying energy transfer processes is complicated by the fact that the polymer, e. g. , polystyrene or polyvinyl toluene, has a relatively high fluorescent quantum yield. This enhances the possibility of a radiative transfer mechanism. For the polystyrene-anthracene system, Koski (18) suggested a radiative transfer mechanism involving polystyrene fluorescence followed by absorption by anthracene. The anthracene molecule then emits its characteristic

radiation. However, further study (19-21) soon indicated that such a mechanism could account for only 20% of the luminescent yield of a plastic scintillator.

Swank and Buck (20) carried out an experiment comparing the change in pulse height with solute concentration for different modes of excitation. In one series of experiments the plastic scintillators were excited by either α or β particles. In the other series of experiments the samples were excited by radiation produced by a thin polystyrene disk which in turn was excited by α particles (indirect excitation). From an analysis of their data, the authors concluded that a nonradiative transfer mechanism is operating in the plastic medium. Andreeshev and Rozman (22) quantitatively analyzed the luminescent spectra of thin plastic scintillators and arrived at similar conclusions.

Krenz (14) investigated the polystyrene-anthracene system in detail by use of high-energy excitation. He concluded that at low solute concentration a radiative transfer process predominates, but at higher solute concentrations the transfer is predominantly nonradiative. Birks and Kuchela (23) arrived at similar conclusions for the system 1,1,4,4-tetraphenylbutadiene in polystyrene.

The plastic medium is known to be a heterogeneous mixture of long chain molecules. The role that the polymer chain plays in the energy transfer process is not too well understood. Shimizu, Hirayama, and Okamoto (24) have shown that the transfer efficiency in the system polystyrene - p-terphenyl decreases with an increase in the temperature of polymerization. This is attributed to a decrease in the average length of the polymer chain. Funt and Hetherington (25) found that for average

molecular weights lower than 100 000, the light output depends on the chain length. Krenz (14) suggests that the nonradiative energy transfer process in polystyrene-anthracene is an intramolecular process. The increase in efficiency with solute concentration is partly explained by anthracene being chemically bound to the polymer chain. Avivi and Weinreb (26) measured the transfer efficiencies for two different types of solution. One solution was a polystyrene plastic scintillator (the solute being anthracene or 2,5-diphenyloxazole) dissolved in ethyl acetate. The other consisted of the particular solute added to a solution of polystyrene in ethyl acetate. In the former solution, chain attachment was possible; in the latter solution chain attachment was highly improbable. The authors concluded that chain attachment is not necessary for increased efficiency. Also, while anthracene is attached to the polymer chain, nonradiative energy transfer may still be an intermolecular process. Brown, Furst, and Kallmann (27) studied the effect that naphthalene has on the energy transfer process in polystyrene and polymethyl-methacrylate. They report that naphthalene enhances the energy transfer process in the rigid medium in a manner similar to that found for the liquid media. The authors were not able to distinguish between a migration process, involving transfer along the polymer chain, and a single-step process involving relatively long distances. They tentatively concluded that perhaps a combination of both processes were involved.

An investigation of the lifetimes of the excited molecules can be an important means of helping to clarify the mechanism by which energy is transferred to the fluorescent solute. Lifetime studies on p-terphenyl in polystyrene excited by high-energy radiation have shown that the decay

does not follow an exponential decay law. (28) Comparative studies of p-terphenyl in toluene show that the luminescent decay does follow an exponential decay law. Thus we see an important difference between the rigid and the liquid medium. Kilin and Rozman (29) studied the photofluorescent lifetime of 1,1,4,4-tetraphenylbutadiene and 1,3,5-triphenyl- Δ^2 -pyrazaline in polystyrene. Using a phase fluorometer, they found that for direct excitation of these solutes the decay does obey an exponential decay law. There is an increase in the lifetime of these solutes with an increase in concentration. This is what one would expect if self-absorption processes are operating.

Recently Basile and Weinreb (30) have made a detailed study on the lifetimes of anthracene and 9,10-diphenylanthracene in polystyrene. Samples were excited both by uv and electron excitation. The authors analyzed the shapes and duration of the light pulse that was produced by these different modes of excitation. By such an analysis it was shown that a radiative transfer process takes place at low solute concentrations. At higher solute concentrations the much faster nonradiative transfer process predominates. However, data obtained by the two modes of excitation did not differentiate between an intermolecular and an intramolecular process of energy transfer.

The shape of the light pulse obtained for both electron and uv excitation did not obey a simple exponential decay law. For dilute solutions, they could successfully describe the shape of the light pulse as a cascade of two exponentials. Essential to their analysis was the assumption that the fluorescent decay of polystyrene follows an exponential decay law. (28) Numerous measurements on electron excitation of pure polystyrene have shown this to be true for at least two thirds

of the decay curve. Kilin and Rozman (31) have published data showing that the luminescence of polystyrene does not decay according to a simple exponential law. These authors, using a phase fluorometer for their measurements, observed a change in lifetime with a change in modulation frequency. The difference between these results may be due to the different techniques used. However, the lifetime values that Kilin and Rozman report for polystyrene are 10-25% lower than values obtained by Basile (32) for both thick and thin samples. The reason for the discrepancies in the lifetime studies is not understood at this time. It is obvious that more study is needed in this field to help understand the energy transfer process.

The work on energy transfer can be summarized briefly as follows. The transfer of energy from the excited solvent molecule to the solute molecule is concentration dependent. A radiative transfer takes place at low solute concentration. As the concentration increases the transfer becomes predominantly nonradiative.

Some attempts have been made to see how the polymer chain is involved in the transfer process, if indeed it is involved at all. This has not been too successful. Thus far it has not been possible to distinguish between a migration (intramolecular) process or a single-step jump (intermolecular) process of energy transfer.

4. APPLICATIONS OF PLASTIC SCINTILLATORS

While plastic scintillators form a somewhat special group among organic scintillators, they are widely used in the detection of ionizing radiation. The increasing use of plastic scintillators has demonstrated that these detectors have great value both in scientific experimentation

and for technical measurements. A very brief discussion of a few of their uses will be given.

Plastic scintillators are widely used for β -particle counting. (33, 34) Their mechanical properties adapt them to the construction of very sensitive well-type counters. One use of these well-type counters has been the measuring of exchangeable K^{42} in man. (35) For soft β -radiation, it was reported that it is possible to obtain counting efficiencies two to three times as great as that obtained by use of gas counters.

Plastic scintillators can also be used in coincidence circuits, for β spectrometry, and also for studying nuclear transformations. For studying nuclear phenomena a serious shortcoming is the low cross section for the photoelectric effect. By using thin films it is possible to count fission fragments. Thin scintillators in conjunction with thick scintillators have proved useful for particle identification. (36) Since they have a high hydrogen content, plastic scintillators can also be used for studying fast neutrons.

Large plastic scintillators are being used more and more in the study of cosmic rays. (37) In contrast, thin filaments of plastic scintillators can act as light pipes and a counter made up of a large number of these filaments can serve to register particle tracks. (38-40)

There are a number of distinct advantages to using plastic scintillators as detectors. They are fairly simple to prepare in a large variety of sizes and shapes. They are fairly easy to machine and have high mechanical strength. They possess good optical properties and good temperature stability. Plastic scintillators have been used in

the temperature range from -190°C to $+70^{\circ}\text{C}$. They require very little in the way of special packaging to protect them from adverse effects of the atmosphere. Also plastic scintillators can be used inside vacuum equipment.

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