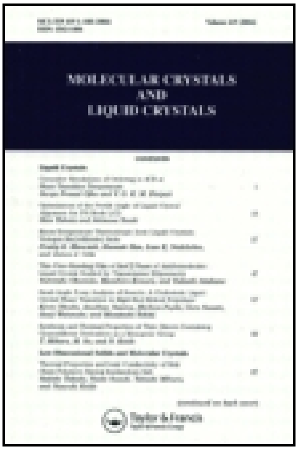

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A Model for the Nonlinear Response of Plastic Scintillators to Intense Weakly Ionizing Radiation†

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Abstract—Plastic scintillators are less efficient to heavily ionizing particles than to weakly ionizing fast electrons. Nonlinear behavior has also been observed on a macroscopic scale when the flux rate of electrons is sufficiently intense. A phenomenological model to explain the latter effect is herein presented. The model postulates that an ionizing particle absorbed in the fluor deactivates a volume surrounding the particle track. The affected volume recovers with a rate constant k. For 100 kV electrons in a beam $j(t)$ electrons/cm^2-sec the fraction of the quenched fluor volume δ is found to be given by the expression

$$\delta = e^{-w} \int_0^t e^{w} j(t) dt$$

where

$$w(E) = \int_0^t [\sigma j(t) + k] dt$$

and

$$\sigma = (3.3 \pm 0.8) \times 10^{-13}\ \mathrm{cm}^2,\ k \sim 3 \times 10^3\ \mathrm{sec}^{-1}.$$

The fluorescence emission is $l = l_0[1 - \delta(t)]$ where $l_0 = sj_0$ and s is the limiting fluor efficiency as $j \to 0$. The susceptibility to quenching of the fluor used in this experiment is $G = 4.8 \times 10^{-14}\ g$/MeV which is equivalent to 28,000 monomer units of styrene per 100 eV of energy absorbed. It is suggested that this effect may be due to excitons absorption by impurities in some local crystalline order.

1. Introduction

We have used plastic scintillators in radiation detectors for many years for instrumenting nuclear weapons tests. The radiation from

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these sources is very intense, and we have noticed that sometimes the detector current falls below the value expected from a calibration using a relatively weak radiation source such as Co^{60} and comparison with other linear detectors. This effect, known to us as " fluor saturation " could not be traced to electronic components of the detector system. Moreover, calibrations subsequent to exposures in which fluor saturation was observed did not reveal any permanent damage to the fluor. The plastic material of interest to us was composed of 2.5% *p*-terphenyl (PT) and 0.03% tetraphenylbutadiene (TPBD) by weight in polystyrene (PS).

Fluor saturation has also been clearly seen using 50 nsec wide 30 MeV electron pulses for beam intensities of $\sim 1 A/cm^2$. The advent of intense radiation sources, such as flash X-ray machines, has made this fluor saturation effect of general interest. A search of the literature, particularly on the scintillation in plastic scintillators, has not revealed any immediately relevant data or theory which explains the effect. Therefore, a phenomenological approach was taken to predict fluor behavior under intense radiation, which, although the details of the mechanism have yet to be discovered, would still be useful to experimenters.

2. Derivation of the Model

Evidently, the quenching action in fluor saturation persists for times which are long compared to the duration of excited states of the various components in the fluor. The scintillation decay time for the material examined is ~ 3 nsec and the radiation intensity level sufficient to produce saturation is much too small to maintain an appreciable fraction of electronically excited states. Also, the absorbed dose which produces saturation is energetically incapable of yielding enough radiation by-products (chromophores) which might compete with the acceptor molecules (PT) for the donor (PS) excitation energy. Opacity effects are also ruled out for the same reason.

It is reasonable to assume that the quenched volume is confined to a small region surrounding the particle track and, for lack of any other information, recovers with a rate proportional to the amount of quenched volume.

At a given point (s) in the track, the volume quenched is proportional to the energy loss rate of the particle (dE/dS) MeV/cm. This volume can be expressed as

$$dV = G/\rho \left(\frac{dE}{dS}\right) ds \text{ cm}^3 \tag{1}$$

where dV is the desensitized volume in a thin slab of thickness ds normal to the track. The quantity G is the susceptibility of the fluor to quenching, in units of reciprocal absorbed dose g/MeV, and ρ is the density of the material (g – cm^{-3}). The radial distribution of this quenched volume is unknown, but we will assume that there is some equivalent area $\sigma(s)$ cm^2 at s surrounding the track in which the fluor is temporarily, but completely, insensitive to further excitation. Thus

$$\sigma(s) = G/\rho \left(\frac{dE}{dS}\right) \text{ cm}^2 \tag{2}$$

For monoenergetic electrons, $\sigma(s)$ is averaged along the electron path length,

$$\overline{\sigma(s)} = \sigma = \frac{GE_0}{\rho R} \tag{3}$$

where E_0 is the incident electron energy. This value is the operational definition of the column " cross section ".

A high-intensity beam produces many of these microscopic columns, some of which may overlap. The time rate of change of the total quenched volume due to a homogeneous beam $j(t)$ (electrons-cm^2-sec^{-1}) has the form

$$V = P_q(t)\, \sigma\, R\, a\, j(t) - kV \tag{4}$$

where $P_q(t)$ is the probability that a column formed by an electron incident at time (t) will not overlap with columns formed earlier. (For this model, overlapping columns cannot further reduce the sensitivity in the overlap region since a single column has been defined as the equivalent volume which is completely quenched by one electron.) The initial active volume is aR cm^3 where a is the area of the beam and k is a recovery rate constant. Clearly, P_q is equivalent to the fraction of the unaffected volume,

$$P_q(t) = [aR - V(t)]/aR.$$

If we define $\delta(t)$ as the fractional quenched volume,

$$\delta(t) = \frac{V(t)}{aR}, \tag{5}$$

Eq. (4) becomes

$$\delta(t) = [1 - \delta(t)]\,\sigma j(t) - k\delta. \tag{6}$$

With the initial conditions δ and $q = 0$, where

$$q(t) = \int_0^t j(t)\,dt \text{ electrons/cm}^2,$$

we find

$$\sigma = (d\delta/dq)_0. \tag{7}$$

So it appears possible to measure the value of G in Eq. (3) by an experimental determination of the initial slope of the δ versus q curve. Moreover, this method should give a value independent of the particular recovery dynamics.

The solution of Eq. (6) is

$$\delta = e^{-w} \int_0^t e^{w} j(t)\,dt \tag{8}$$

where

$$w(t) = \int_0^t [\sigma j(t) + k]\,dt.$$

In terms of the absorbed dose of electrons $q(t)$,

$$w(t) = \sigma q(t) + kt.$$

For the special case where $j(t)$ is a step function of amplitude j_0,

$$\delta_{\text{step}} = \frac{\sigma j_0}{\sigma j_0 + k}\left[1 - e^{-(\sigma j_0 + k)t}\right]. \tag{9}$$

The first term is the equilibrium value of δ_{step} for a long square pulse. For short pulses, where $(\sigma j_0 + k)t \ll 1$, $\delta(t)_{\text{short}} = \sigma q(t)$.

It can also be seen that for low currents where $\sigma j_0 \ll k$, δ is always small, so that the light emission is linear. The fluorescence emission is

$$l = l_0[1 - \delta(t)] \text{ where } l_0 = s j_0 \tag{10}$$

and s is a constant, determined by a calibration.

3. Experimental Procedure

The plastic scintillator samples were prepared by a bulk polymerization process developed at this Laboratory, as described by Wouters.(1) After fluorescent chemicals were added, the plastic scintillator was bulk thermally polymerized (autocatalytically) at 150 °C for 24 hr in a nitrogen atmosphere. Zinc stearate (0.01%) was added as a mold releasing agent. The styrene contained 0.1% inhibitors added by the manufacturer. The mold was a 2.5 gal Pyrex bottle yielding a 6 × 10 in. ingot. Specimens were machined from the ingot. The molecular weight range was about 50000 to 200000.

In addition to polystyrene, the polymer will contain residual monomer, impurities such as ethyl benzene and aldehydes, and low molecular weight polymers; e.g., dimers and trimers. There is no reason to believe that fluor saturation is a peculiar property of the samples in this experiment, because unpublished results with other commercial plastic scintillators (NE–102 and Pilot B) indicate the same saturation effect when 12 MeV electrons are transmitted through the samples. The pulsed electron beam was only a few μsec long and did not furnish much information on the duration of the quenching.

The radiation source was a 500-μsec nearly square pulse of 100 kV electrons delivered by a small electrostatic accelerator,(2) which was originally designed to emit intense short bursts of electrons (<1 nsec wide) for impulse response studies. For this experiment, it was modified to deliver 500-μsec nearly square pulses (with a rise time of 0.6 μsec) to allow the expected long-lasting transient desensitivity to be seen easily. The modification resulted in a sagging of the current because of the limited capacity of the electron gun plate power supply, and led to applying polynomial fits to the data.

A cross-section view of the experimental arrangement mounted on the end of the accelerator tube is shown in Fig. 1. The test fluor sample was a disc 17.8 mm in diameter and 3.18 mm thick. The beam was stopped in the fluor. The top surface toward the beam was made conductive by a thin vapor plating of Al. This surface was connected to the upper display of a Tektronix type 551 dual beam oscilloscope. The Al-covered insulated disc acted as a Faraday cage, providing the means for directly measuring the electron beam

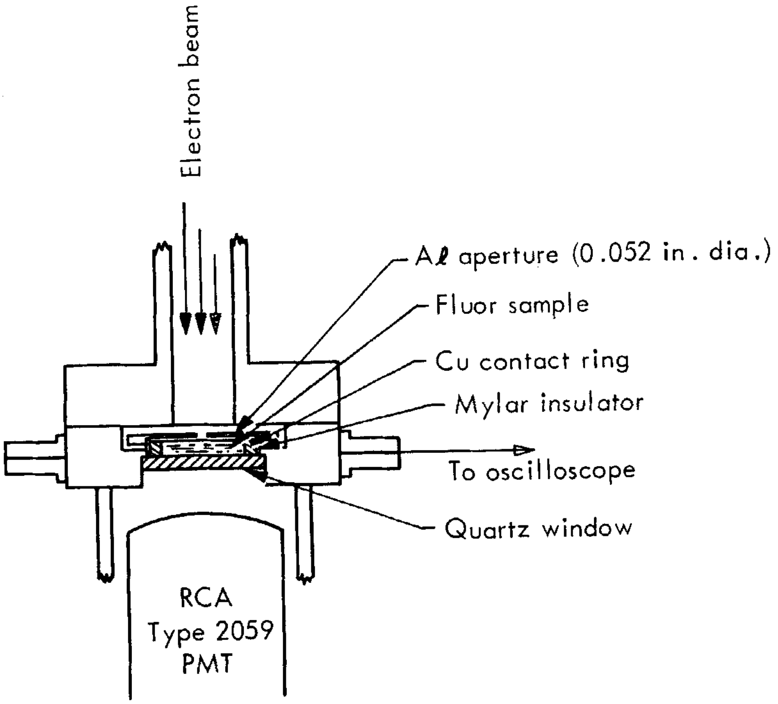
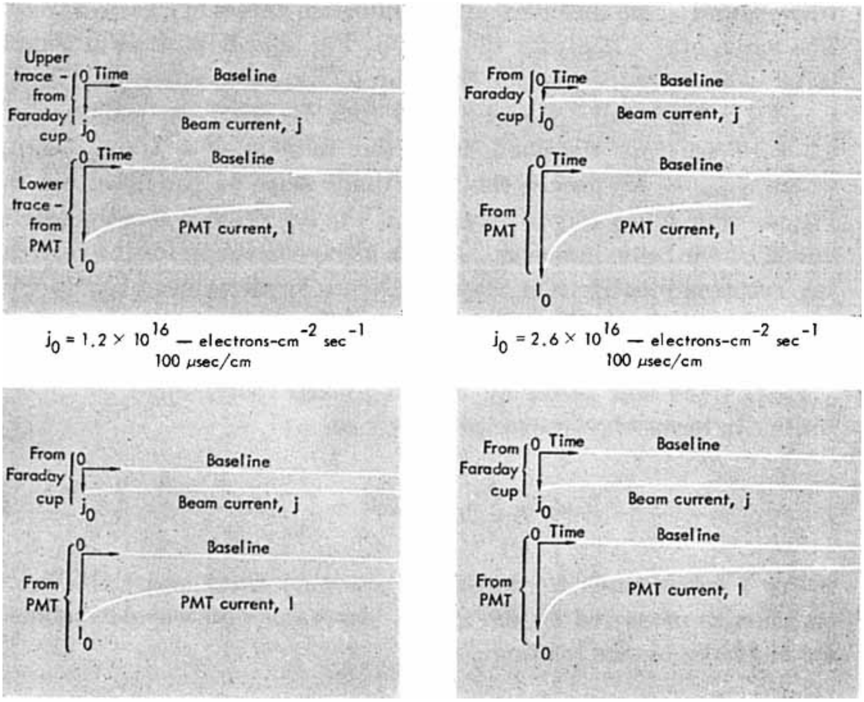


Figure 1. Cross-section view of experimental arrangement mounted beneath the accelerator tube. The fluor sample was aluminized on its top surface to act as a beam current monitor.

current through the 1.32-mm diameter aperture placed closely above. Since the surface of the fluor was connected to ground potential through a 50 Ω resistor, the electrons did not see any appreciable retarding potential due to space charge buildup in the fluor. The photomultiplier tube (PMT) output was displayed on the lower trace, and also terminated with a 50 Ω resistor at the scope. Both signals were negative.

Figure 2 shows some oscillographs in which the PMT signal, which is proportional to the light emitted by the fluor, can be seen to decrease as the dose increases, but tending toward progressively lower equilibrium values depending on the dose rate, after a few hundred microseconds from the start of the pulse. The PMT was tested and found to have a linear response to 500-μsec square light pulses up to the highest levels of output encountered in the experiment.



$j_0 = 1.2 \times 10^{16}$ — electrons-cm^{-2} sec^{-1}
100 μsec/cm

$j_0 = 2.6 \times 10^{16}$ — electrons-cm^{-2} sec^{-1}
100 μsec/cm

$j_0 = 4.4 \times 10^{16}$ — electrons-cm^{-2} sec^{-1}
20 μsec/cm

$j_0 = 1.4 \times 10^{17}$ — electrons-cm^{-2} sec^{-1}
20 μsec/cm

Figure 2. Typical oscillographs recorded on the dual beam oscilloscope from the experimental arrangement in Fig. 1. The upper pair of traces in each photograph show the zero-volt baseline (recorded shortly before the pulse) and the negative signal from the fluor acting as a Faraday cup. The lower pair of traces in each photograph are the 0-volt baseline and the PMT signal (also negative) due to light emitted by the fluor. Both signals were fed to 50 Ω terminal resistors at the scope input via 50 Ω coaxial cables.

4. Experimental Results

In general, the light emission pulse has the form predicted by Eq. (10). The relaxation of the quenching may actually be more complex than the assumptions which led to Eq. (8). No attempt has been made to analyze the recovery dynamics in detail.

From Eqs. (9) and (10),

$$l - l_\infty = (l_0 - l_\infty)\, e^{-(\sigma j_0 + k)t} \tag{11}$$

where l_0 and l_∞ are the initial and equilibrium values of l, respectively. The value of $(l - l_\infty)/l_0$ for the data of Fig. 2(*a*) is plotted in Fig. 3 (after a linear correction for the drop in the beam current). Using $\sigma = 3.4 \times 10^{-13}\,\mathrm{cm}^2$, $j_0 = 1.2 \times 10^{16}\,\mathrm{cm}^{-2} - \mathrm{sec}^{-1}$ a value $k = 3.3 \times 10^3\,\mathrm{sec}^{-1}$ is obtained from the relation $k = 1/\tau_{\mathrm{meas.}} - \sigma j_0$, where $\tau_{\mathrm{meas.}} = 136\,\mu\mathrm{sec}$ is the logarithmic slope of the fitted line in Fig. 4. For much larger values of j_0 the log slope is mostly determined by the beam intensity. Also, a linear correction for the current sag becomes invalid. On the other hand, small values of j_0 do not give a large effect. Therefore, k can be estimated only for a few traces in this experiment.

Each trace was fitted by a least-squares polynomial computer routine in terms of power series of the form

$$j(t) = \sum_0^n j_i t^i, \quad l(t) = \sum_0^n l_i t^i$$

where j corresponds to the upper (current) trace and l the light emission as measured by the PMT. The value of σ was determined for 28 traces by the relation

$$\sigma = \left(\frac{\mathrm{d}\delta}{\mathrm{d}q}\right)_0 = \frac{1}{I_0}\left(\frac{j_1}{j_0} - \frac{l_1}{l_0}\right),$$

where I_0 is a conversion factor relating the current density to the trace deflection and has the value $I_0 = 8.43 \times 10^{18}\,j_0$ is measured in volts and t in seconds. The results are summarized in Fig. 4.

The value of σ is determined to be $\sigma = 3.3 \pm 0.8 \times 10^{-13}\,\mathrm{cm}^2$. There is no apparent correlation of σ with intensity j. For 100-keV electrons, an average energy loss rate of 6.95 MeV $\mathrm{g}^{-1}\,\mathrm{cm}^{-2}$ was computed using the results of Berger and Seltzer.(3) Equation (3) then gives the value $G = 4.8 \times 10^{-14}$ g/MeV which is equivalent to the quenching of 28,000 monomer units of styrene (mol. wt 104.14) per 100 eV of energy absorbed. Actually, σ was determined not at $t = 0$ but at a later time $\tau_r = 0.8\,\mu\mathrm{sec}$ equal to the rise time of the beam pulse. The small dose absorbed within this interval is not expected to affect the results within the accuracy of this experiment. The accuracy of these measurements is indicated by the statistical spread of the points in Fig. 4.

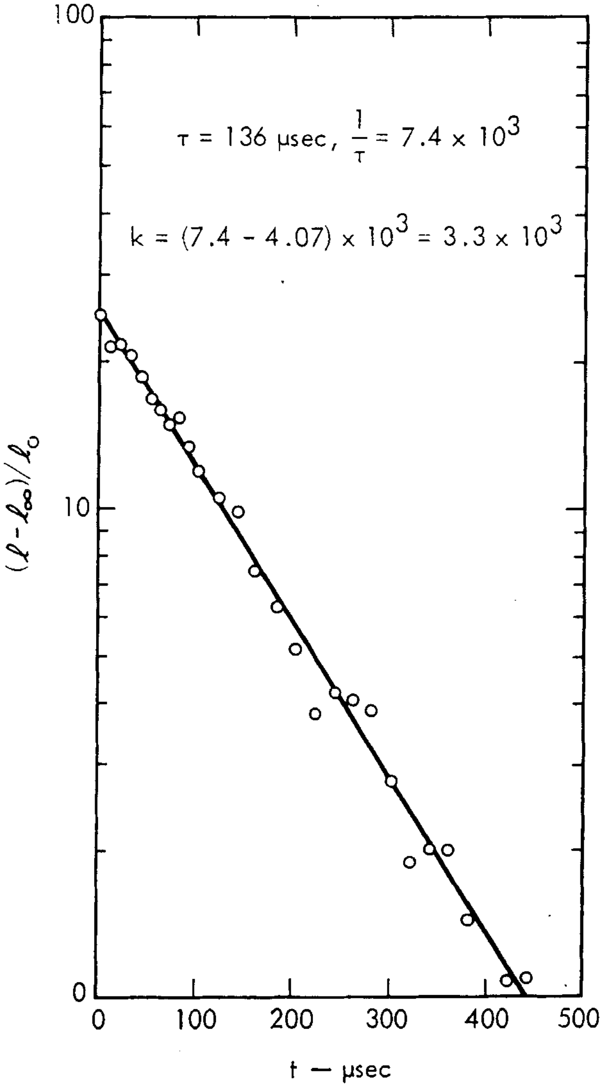


Figure 3. The function $(l - l_\infty)/l_0$ plotted from the data of Fig. 2. A linear correction for the sag in the beam current was made by subtracting an appropriate amount from the PMT signal. The log slope of the fitted line gives a value $k = 1/\tau_{\text{meas.}} - \sigma j_0 = 3.3 \times 10^3$ sec^{-1} using $\sigma = 3{\cdot}4 \times 10^{-13}$ cm^2.

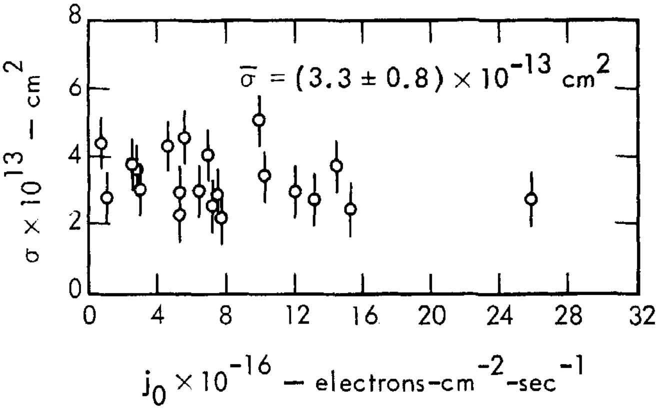


Figure 4. Values of σ computed according to Eq. (7) plotted as a function of the initial electron current density j_0 electrons–cm^{-2}–sec^{-1}.

5. Discussion

In deriving a model for the fluor saturation effect, it was found useful to make an oversimplified and unrealistic assumption about the radial distribution of the quenched volume. The degree of quenching not only decreases radially but, for electrons, is not uniform along the track. Much of the ionization is contained in short spurs and blobs which result from low energy delta rays ejected laterally from the path of the electron. However, the validity of the model rests with the assumption that, for the purpose of predicting saturation effects, an equivalent totally quenched volume exists for any real distribution. Without some simplifying assumptions, the analysis would be unnecessarily complicated, or perhaps not possible since the actual distribution is not known.

The unexpectedly large degree of quenching raises some questions concerning the range of energy transfer from the PS to the quencher. Only a small percentage of the total energy could be expected to result in mobile electronic energy states, so the quenching of 28000 monomer units by 100 eV is a lower limiting value.

The scintillation mechanism in organic fluors is believed to involve a mainly nonradiative dipole-dipole resonance transfer from the solvent to the solute as proposed by Forster(4) and Dexter(5) and verified by others.(6,7) Most methods for measuring the nonradiative transfer efficiencies have utilized ultraviolet light to excite the first singlet band of the donor. Brown, Furst, and Kallman(8) associate fluorescence quenching in plastics with absorption of this energy by nonfluorescent centers. However, the pulse radiolysis absorption spectra ($g\epsilon = 6 \times 10^4$ where g is the 100-eV yield and ϵ the extinction coefficient at 440 mμ peak) of 0.024M p-terphenyl in PS measured by Ho, Siegel, and Schwarz(9) show that quenching by radiation by-products to the degree found in this present experiment is not likely without assuming highly mobile energy states, as hypothesized in Ref. (8).

The assumption of first-order kinetics for recovery of the quenching should be regarded only as a crude first approximation. However, for radiation pulses that are short compared to the overall recovery time, the desensitized volume is proportional to the absorbed dose and does not depend much on the recovery rate. The quenching species has not been identified but appears to be of much shorter duration than the complex decaying 20-msec initial half-life component found by Ho, Siegel, and Schwarz(9) by pulse radiolysis of PT dissolved in PS.

The intramolecular energy transfer probability by dipole-dipole resonance in PS has been calculated by Hirayama(10,13) to be $(0.88)^n$ where n is the number of monomer units participating. The process terminates upon forming an eximer with another suitably oriented monomer unit. Berlman(11) has calculated an eximer quantum yield of 0.03 for 10 g/liter PS in cyclohexane. This would indicate a transfer over about 27 monomer units before eximer formation, and could not account for the magnitude of the effect observed in the present experiment. Also, it does not seem likely that energy could be transferred only along the polymer chain by any other mechanisms, since the average molecular weight of the PS is insufficient to involve a large enough number of monomer units in the transfer process.

However, it is still possible that, under high energy excitation, higher delocalized electronic levels are produced. In this connection the results of Leibowitz and Weinreb(12) are of interest. They find the fluorescence yield and the spectral emission depend strongly on the ultraviolet excitation wavelength in the region 2850 to 548 Å. In some samples of solid PS the fluorescent quantum yield was a factor of 8 higher for 580 Å than at 2850 Å. Moreover, the yields varied from sample to sample depending on mode of preparation, surface treatment and application of pressure. This behavior is markedly different from polystyrene in cyclohexane where the yield is found to decrease continuously for shorter wavelengths. This dependence on the state of aggregation of the PS indicates the existence of a mode of efficient energy transfer involving higher states whose behavior may be analogous to exciton diffusion in solids.

Crystalline structure in isotactic polymers is common. In particular, large ($\sim 4\ \mu$) crystals of PS have been grown from dilute xylene solutions and from the melt.(13) Solid-state aggregates in bulk polymerized PS apparently have not been established clearly, but Leibowitz and Weinreb(12) infer the existence of such aggregates to explain their results. Macroscopic order also is inferred by them from double-refraction phenomena.

As additional support for this hypothesis, Hirayama, Basile, and Kikuchi(14) have noted that hexachlorocyclohexane is a good quencher of PS + fluor scintillators when β-rays are used (in contrast to ultraviolet excitation). They suggest that this behavior involves interactions from upper excited or ionized states. Thus we may hypothesize that for ionizing radiation perhaps the chief mode of energy transfer is by excitons which can be absorbed by impurities affecting the PS over some local crystalline order.

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