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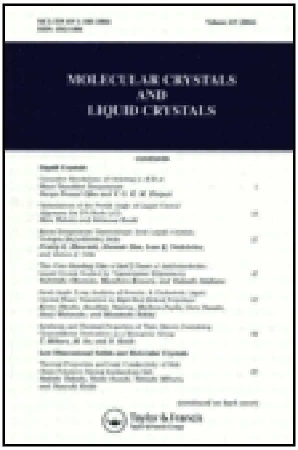

Molecular Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: Frank J. Lynch (1968): New Liquid Scintillators with Faster Response and Higher Efficiency, Molecular Crystals, 4:1-4, 293-301

To link to this article: http://dx.doi.org/10.1080/15421406808082919

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Molecular Crystals, 1968. Vol. 4, pp. 293–301
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New Liquid Scintillators with Faster Response and Higher Efficiency†

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Abstract—The variation of light intensity with the time following excitation by gamma rays has been measured for a quaterphenyl compound whose solubility was enhanced by substitution of alkyl groups. The decay curves, measured by use of a probability-sampling technique, were analyzed to yield preliminary estimates of the time constants τ_1 related to energy transfer from solvent to solute, τ_2 related to the rapidly decaying component from the singlet state, and τ_3 related to the slower component which is probably due to excimers. A solution ($\approx$65 g/liter, $\gamma = 1.12 \times 10^{-2}$) of $1^1, 4^4$-bis(2-butyloctyloxy)-p-quaterphenyl (QP-G12) in toluene shows $\tau_1 \approx 0.05$ nsec, $\tau_2 \approx 1.4$ nsec, and $\tau_3 \approx 11.4$ nsec. The intensity of the slow component (mean life τ_3) is about 20% of that of the fast component (mean life τ_2). This is about a third of the slow/fast ratio measured for 2,5-diphenyloxazone (PPO) in toluene at the same mole fraction. This indicates that QP-G12 does not form excimers as readily as PPO does. For both solutes, measurement shows that τ_1 varies about as the reciprocal of the concentration, as expected. For the same mole fractions, moreover, the fact that the value of τ_1 for QP-G12 is only about half that for PPO indicates that the rate of transfer from solvent molecule to solute is higher for QP-G12 than for PPO. The QP-G12 has a higher light output and shorter τ_1 and τ_2 than the plastic Naton 136 which is commonly used for delayed-coincidence measurements. Preliminary attempts to exploit this advantage led to improved time resolution; for 511-keV gamma-rays, the full width at half maximum was about 0.25 nsec and the slope of the decay curve was $T_{1/2} \approx 0.037$ nsec.

A knowledge of the variation of light intensity with time during a scintillation helps to understand the scintillation process. It can reveal quantitative information about the time for energy transfer from the solvent to the solute, the main fluorescence decay time, and the presence of longer decay times such as those due to excimers.

There are two popular techniques used for studying the scintillation illumination function $I(t)$ in the sub-nanosecond region. In the first, the anode pulse from the photomultiplier is observed by a fast oscilloscope of either the traveling-wave or the sampling type. Since modern fast photomultipliers have a rise time of about 1.5 nsec and a similar decay

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† Work performed under the auspices of the U.S. Atomic Energy Commission.

time, it is necessary to unfold $I(t)$ from the observed pulse which, even when $I(t)$ is a delta function, has a width of several nanoseconds. The second method employs the probability-sampling technique first used by Bollinger.[1] In this method, the rise and decay in the intensity of scintillation light is determined by measuring the distribution of time intervals between the beginning of the scintillation and the emission of individual photoelectrons at the cathode of the photomultiplier that views the scintillation. Two photomultipliers are used. The one closely couplied to the scintillator provides accurate timing of the start of the scintillation. The other photomultiplier, so weakly coupled to the scintillator that only one photoelectron is produced for every 25–30 light flashes, samples the light intensity. The time interval between the start of the scintillation as determined by the closely coupled photomultiplier and the leading edge of the pulse due a single electron in the poorly coupled photomultiplier is measured for many events. The resulting probability distribution combines the effect of the illumination function $I(t)$ and the instrumental response function $P(t)$ of the apparatus. The latter is due largely to the variation in electron transit time in the photomultiplier and can be made relatively independent of the rise and decay times and of the statistical fluctuations in gain.

Figure 1 is a block diagram of the apparatus. The photomultipliers are RCA type 8575 which have a low dark current because of theit bialkali photocathodes. Two signals are taken from each photomultiplier. A fast current pulse from the anode passes directly to the fast descriminators; a slow integrated pulse from the ninth dynode goes to the linear amplifier and from there to the single channel pulse-height analyzer, SCA. The fast tunnel-diode discriminators, which have a fixed dead time of 10 μsec, provide standardized output pulses to the time to-amplitude converter, TAC. The TAC is basically of the overlap type, but provides an output pulse only when input pulse B follows pulse A within the time interval of interest. The window of the SCA in the single-electron channel was set in the middle of the single-electron pulse-height distribution. The window width was about 20% of the mean pulse height. The fast discriminator in this channel, which was set to trigger at about a third of the mean pulse height, provided the start pulse. The window of the SCA in the channel with the closely coupled photomultiplier was set on the upper 30% of the pulse-height distribution due to Compton electrons produced by the gamma-rays from a Cs^{137} source. The fast discriminator in this chan-

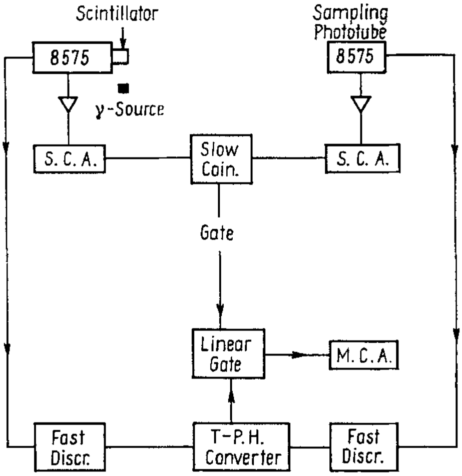

Figure 1. Block diagram of the apparatus for measuring the intensity of scintillation as a function of time.

nel was set to trigger at about a tenth of the mean pulse height in the window. The linear gate opens only when the requirements of both SCA's have been met by the associated linear pulses. When it opens it permits the pulse from the TAC to be stored in the multichannel analyzer.

Figure 2 shows the instrumental response function *P*(*t*), which was obtained with Čerenkov light from a piece of quartz bombarded with beta particles from a Sr^{90} source. The full width at half maximum (FWHM) is about 1.0 nsec and the equivalent half life is $T_{1/2} \approx 0.2$ nsec. A small satellite peak occurs about 24 nsec after the primary peak. The fact that this delay varies about as the square root of the photomultiplier voltage suggests that this peak may be due to photons produced at a later dynode or at the anode. If these reach the photocathode, they may eject a delayed photoelectron. Although this satellite peak is much smaller than the main peaks, its presence can be observed whenever the scintillator has very little slow component. In measurements with organic scintillators, *P*(*t*) should be somewhat narrower than the measured value because of the greatly increased amount of light received by the closely coupled photomultiplier. For convenience and flexibility in adjusting the

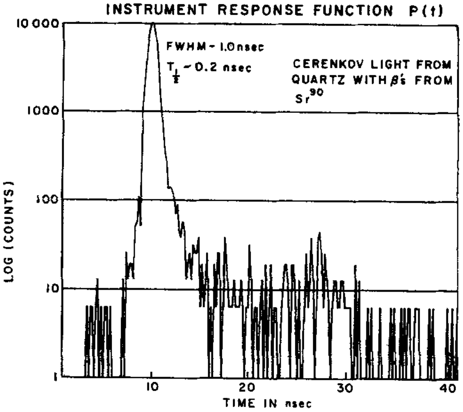

Figure 2. Instrument response function obtained with Čerenkov light produced in quartz by beta particles from a Sr^{90} source.

width of $P(t)$ in the following calculations, $P(t)$ is assumed to be a Gaussian distribution function.

Figure 3 shows the measured time distribution that is obtained on the assumption that the instrumental response is of the form

$$P(t) = \exp\,[(-t^2/2\sigma^2)/(2\pi)^{1/2}] \tag{1}$$

and that the scintillator illumination function is

$$I(t) = [\exp\,(-t/\tau_1) - \exp\,(-t/\tau_2)]/(\tau_1 - \tau_2), \tag{2}$$

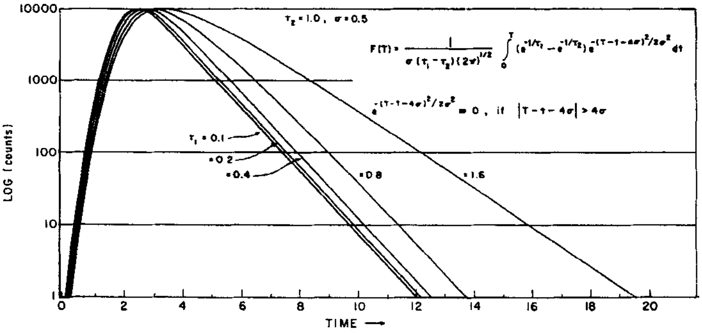

Figure 3. Theoretical shape expected for a Gaussian instrument response function with $\sigma = 0.5$, $\tau_2 = 1.0$ and several values of τ_1.

where τ_1 is the mean life for energy transfer from solvent to solute and τ_2 is the mean life for the decay of the fluoresence. The curves are calculated from the convolution integral

$$F(T) = \int_0^T P(T - t - 4\sigma)\, I(t)\, dt, \tag{3}$$

with $P(t)$ truncated so that

$$P(T - t - 4\sigma) \equiv 0 \quad \text{if} \quad |T - t - 4\sigma| > 4\sigma$$

for $\tau_2 = 1$, $\sigma = 0.5$, and various values of τ_1. The curves are particularly meaningful when the units of time are nanoseconds because $P(t)$ then approximates the instrumental response function shown in Fig. 2. For $\tau_1 < \tau_2$, the slopes of the tails in the semilog plot become equal at long times. However, as τ_1 approaches τ_2, longer times are required before the slope reaches its final value, $1/\tau_2$. When τ_1 exceeds τ_2, the slope at long times approaches $1/\tau_1$. Thus, it can be seen that when τ_1 is comparable to τ_2, it is difficult to get an accurate value of τ_2 without fitting both τ_1 and τ_2.

In analyzing the data, it was assumed that the slow component was due to excimers which were fed by the singlet state. Since at this stage the values of τ_1 and τ_2 were unknown, it was assumed that the time variation of intensity of excimer radiation can be approximated by

$$I(t) = [\exp(-t/\tau_2) - \exp(-t/\tau_3)]/(\tau_2' - \tau_3), \tag{4}$$

where τ_2' is obtained from the slope of the fast component from the semilogarithmic plot of the data. With the approximation (4) substituted in Eq. (3) and with $\sigma = 0.45$ nsec, $F(t)$ was calculated and its amplitude was adjusted so that the number of counts for times long enough for the τ_2 component to be negligible was the same as in the experimental data. Then the slow component was subtracted from the experimental data to leave the fast component. Time distributions were calculated by use of Eq. (3) with different values of τ_1 and τ_2 until the best fit was obtained by visual inspection. More accurate values of τ_1 and τ_2 will be available soon when they can be obtained by minimizing χ^2.

In the following measurements, the samples used were solutions in toluene. After removing the air by flushing with nitrogen, they were sealed in quartz tubes of 5-mm i.d.

Figures 4a and 4b show measurements at two concentrations of 1^1,

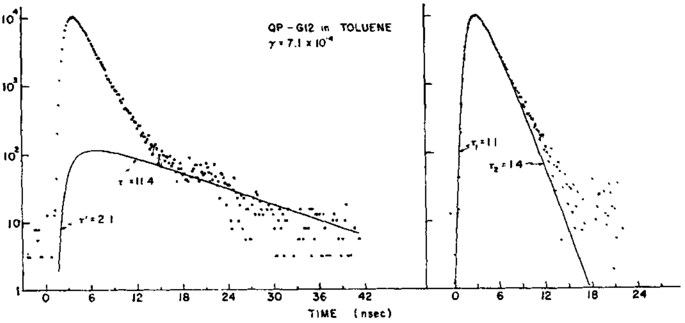

Fig. 4a

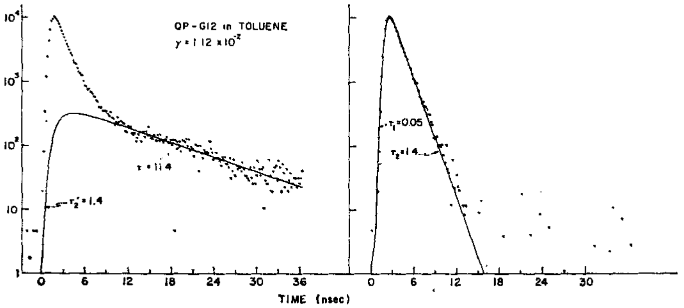

Fig. 4b

Figure 4. Measured intensity of light from QP-G12 in toluene. The curve on the left shows data points with background subtracted and theoretical slow curve superimposed. The curve on the right shows data points following subtraction of slow component and theoretical curve fitted by visual inspection. Fig. 4a, $\gamma = 7.1 \times 10^{-4}$; Fig. 4b, $\gamma = 1.12 \times 10^{-2}$.

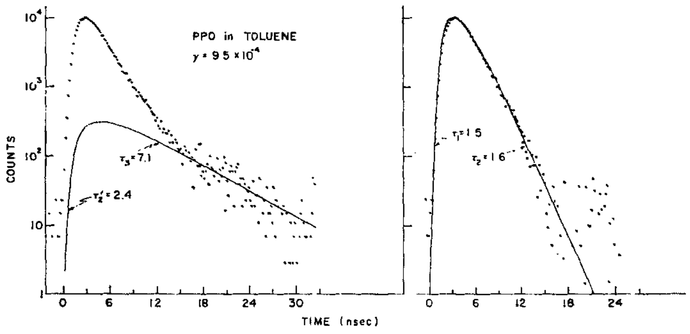

Fig. 5a

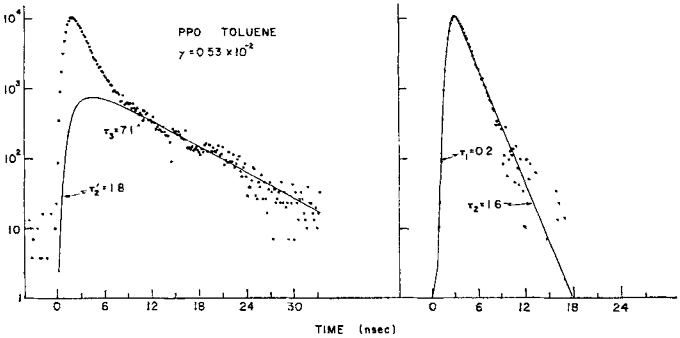

Fig. 5b

Figure 5. Measurements on lower concentrations of PPO in toluene: (a) $\gamma = 9.5 \times 10^{-4}$, (b) $\gamma = 0.53 \times 10^{-2}$.

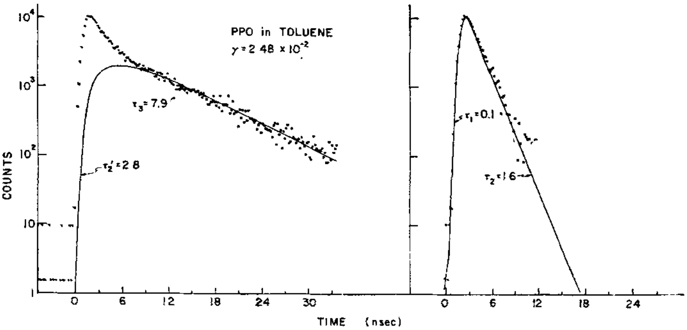

Fig. 6a

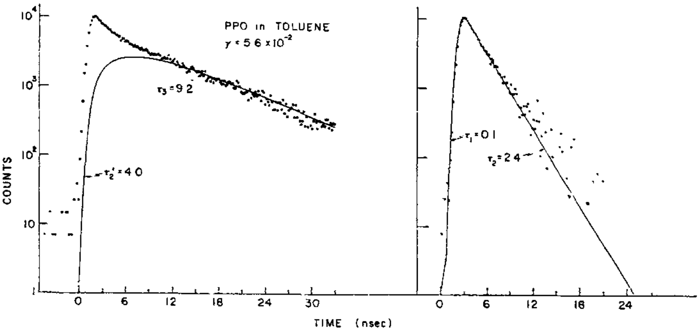

Fig. 6b

Figure 6. Measurements at higher concentrations of PPO in toluene: (a) $\gamma = 2.48 \times 10^{-2}$, (b) $\gamma = 5.6 \times 10^{-2}$.

4^4-bis (2-butyloctyloxy)-*p*-quaterphenyl[2] (*QP*-G12) in toluene for mole fractions $\gamma = 7.1 \times 10^{-4}$ and 1.12×10^{-2}. The theoretical curves were fitted by visual inspection. Figures 5a and 5b show data for fairly low concentrations of 2,5-diphenyloxazole (PPO) in toluene for $\gamma = 9.5 \times 10^{-4}$ and 0.53×10^{-2}. Figures 6a and 6b are for PPO in toluene at high concentrations $\gamma = 2.48 \times 10^{-2}$ and 5.6×10^{-2}). The values of τ_1 and τ_2 obtained for the higher concentrations are less accurate because of errors in subtraction of the slower component (mean life τ_3). One would expect τ_2 to decrease with increasing excimer radiation, but this may be compensated by the apparent increase due to absorption and reradiation of the singlet radiation. The latter effect was observed with QP-G12 in toluene at $\gamma = 1.12$. The value of τ_2 increased by about 10% on enlarging the sample diameter from 5 mm to 2 cm. The experimental results are summarized in Table 1.

These preliminary results indicate that τ_1 is inversely proportional to γ. At the same value of γ, the value of τ_1 for QP-G12 is about half the value for PPO. This indicates that the QP-G12 molecule is excited by the excited solvent molecule more efficiently than is the PPO molecule. The ratio of slow to fast component increases with γ for both solutes. At a given γ there is only about a third as much slow component with QP-G12 as with PPO. The formation of excimers in QP-G12 is certainly inhibited. Further experiments are required to demonstrate whether or not this slow component in QP-G12 is, in fact, due to excimers.

For delayed-coincidence measurements in the sub-nanosecond region, it has been customary to use the plastic scintillator Naton-136 in order to obtain the best results. However, QP-G12 in p-xylene (18 g/liter) gives

TABLE 1. The time constants τ_1, τ_2, and τ_3 for the three components of the scintillation and the ratio of the intensities of the slow (τ_3) and fast (τ_1 and τ_2) components for different concentrations γ of the two solutes.

Solute	γ	τ_1 (nsec)	τ_2 (nsec)	τ_3 (nsec)	Slow/fast
PPO	9.5×10^{-4}	1.65	1.6	7.1	0.09
	5.3×10^{-3}	0.2	1.6	7.1	0.31
	2.5×10^{-2}	0.1	1.6	7.9	1.01
	5.6×10^{-2}	0.1	2.4	9.2	1.4
QP-G12	7.1×10^{-4}	1.1	1.4	11.4	0.05
	1.12×10^{-2}	0.05	1.4	11.4	0.2

off about 75% more light, and has shorter τ_1 and τ_2. For this reason it should provide considerably better time resolution. A γ-γ coincidence measurement of the 511-keV positron annihilation radiation was made with two quartz containers, 2 cm in diameter × 1 cm deep, filled with QP-G12 in p-xylene (18 g/liter). The resultant coincidence curve showed FWHM $\approx$ 0.25 nsec and $T_{1/2} \approx$ 0.037 nsec. Although there was no extensive effort to optimize the time resolution, this compares favorably with the values FWHM $\approx$ 0.43 nsec and $T_{1/2} \approx$ 0.048 nsec which Schwarzschild obtained with Naton-136 and the 56 APV photomultiplier.

The measurements would not have been possible without the samples so generously provided by Herman O. Wirth and Donald L. Horrocks. Also, I am indebted to Isadore B. Berlman for preparing samples and for several informative discussions about organic scintillators. The helpful and timely assistance of Leonard E. Olson, Jr., in programming and analyzing the data is gratefully acknowledged.

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