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Photostability of pyrromethene 567 laser dye solutions via photoluminescence measurements

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Abstract

The effects of antioxidant addition and concentration on the photostability of methanol solutions of the pyrromethene laser dye 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-difluoroborate complex (PM-567) were investigated. Specifically, methanol solutions of PM-567 were irradiated with 532 nm Nd:YAG laser pulses (2nd harmonic), and the photoluminescence measured as a function of accumulated laser pulses. The decrease in the photoluminescence-to-initial photoluminescence ratio with accumulated laser pulses was measured as a function of antioxidant addition and dye concentration. The addition of antioxidants, 1,4-diazabicyclo[2.2.2] octane (DABCO) and sodium azide (NaN_3), resulted in a dramatic enhancement of photostability, whereas only nominal enhancement was observed upon *n*-propyl gallate addition. Over the concentration range 6×10^{5} to 5×10^{4} M, dye-photostability was virtually concentration independent, with only a small enhancement at lower concentrations. The normalized photostability, the half-life of accumulated energy per mole of dye, could not explain the concentration dependence of photostability. Reasons why the normalized photostability fails to explain the concentration trends are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Photoluminescence; Photostability; Solid-state dye laser; Pyrromethene difluoroborate complex; Photochemical layer; Singlet oxygen

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1. Introduction

Organic dyes are commonly used in photonic applications, including optical discs (CDs, DVDs) [1], light emitting diodes [2,3], optical imaging [4] and solid-state dye lasers [5–10]. Pyrromethene dyes in particular have been successfully employed in solid-state dye lasers, due to their low triplet extinction coefficients and high quantum efficiencies. An organic light-emitting device (OLED) utilizing an indium tin oxide electrode coated with 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-difluoro borate complex (PM-567) and 8-hydroxy quinoline aluminum salt, has been reported [11].

Utilizing a very similar sandwich electrode architecture, the photocurrent generated from 532 nm-irradiated polymer films containing PM-567 has been measured [1]. In that study, it was demonstrated that the application of an external electric field accelerated the decrease in the photoresponse of PM-567/poly(methyl methacrylate) (PMMA)

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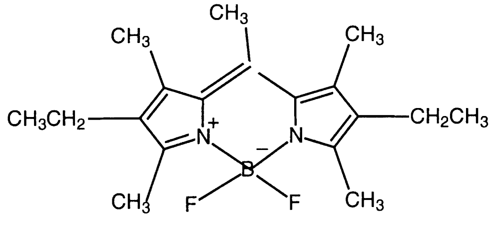

PM-567

films. This has implications for OLED photostability, since OLEDs and photovoltaics utilize similarly constructed sandwich electrodes and related mechanisms: current → light for OLEDs and light → current (voltage) for photovoltaics.

Low photostability, however, remains a chief concern for polymer-dispersed pyrromethene dye lasers. There are several factors that contribute to the photodegradation of dyes embedded in polymers. One of the major reasons for pyrromethene dye photodegradation in solid-state dye lasers is self-sensitized photooxidation via singlet oxygen [7]. This process is illustrated by Eqs. (1)–(7), where $D = {}^1D_0$ singlet ground state laser dye.

$$D + h\nu \xrightarrow{k_1} {}^1D^* \tag{1}$$

$$k_1 = \frac{\sigma I}{h\nu},$$

σ = absorption cross section, I = laser fluence per unit time, υ = frequency of laser light = 5.64×10^{14} s^{-1} for 532 nm light, h = planck's constant.

$$^1D^* \xrightarrow{k_2} {}^1D(+h\nu) \tag{2}$$

$$^1D^* \xrightarrow{k_3} {}^3D \tag{3}$$

$$^3D + {}^3O_2 \xrightarrow{k_4} {}^1D + {}^1O_2 \tag{4}$$

$$^1O_2 + D \xrightarrow{k_5} DO_2 \tag{5}$$

$$^1O_2 + D \xrightarrow{k_6} {}^3O_2 + D \tag{6}$$

$$^1O_2 \xrightarrow{k_7} {}^3O_2 \tag{7}$$

$$^1O_2 + Q \xrightarrow{k_Q} {}^3O_2 + Q^* \text{ or products} \tag{8}$$

Eq. (8) suggests that the addition of singlet oxygen quencher (Q) may lead to enhanced dye photostability. This has been observed by Rahn and coworkers for PM-567 in methanol, ethanol and poly (methyl methacrylate), using NaN_3 and 1,4-diazabicyclo [2.2.2] octane (DABCO) as singlet oxygen quenchers [7,8]. In their experiments stimulated emission (lasing) was measured. In the present study, the work of Rahan and coworkers has been extended to the evaluation of the antioxidant, *n*-propyl gallate, by observing spontaneous emission. In addition, the dye concentration dependence of photostability has been assessed, enabling an evaluation of the previously reported concentration invariance of the *normalized photostability*, a concept introduced by Rahn and coworkers [7,8].

2. Experimental

2.1. Sample preparation

PM-567 was dissolved in methanol to give a 5×10^{-4} M solution. Methanol solutions containing antioxidant:dye mixtures (100:1 mole ratio) were prepared using PM-567 in combination with 1,4-diazabicyclo[2.2.2] octane (DABCO), NaN_3, and *n*-propyl gallate.

2.2. Photoluminescence measurements

Quartz cuvettes containing 0.7 ml of dye/antioxidant mixtures in methanol were irradiated by 532 nm light via the second harmonic of a Nd:YAG laser. A monochromator allowed 592-nm emission to be detected by a photomultiplier tube (PMT). The amplified PMT response was averaged by a boxcar integrator. A pump-probe technique was utilized in which the sample's fluorescence intensity was measured at discrete time intervals for 10 s with a low laser fluence (incident energy per unit area) of 21 mJ cm^2 $pulse^{-1}$. The irradiation occurred during the time between measurements utilizing a high pump laser fluence of 176 mJ cm^2 pulse^{-1}. The low probe energy in combination with filters placed on the monochromator entrance slits, minimized scattered light contamination of the signal. The absence of a photoluminescence signal for a methanol blank confirmed that scattered light was negligible under the present experimental conditions.

3. Results and discussion

3.1. Antioxidant dependence

Fig. 1 shows light intensity plots as a function of laser pulses, providing comparisons of air saturated 5×10^{-4} M PM-567/methanol solutions with 5×10^{-2} M DABCO, 5×10^{-2} M NaN_3, and 5×10^{-2} M *n*-propyl gallate. The DABCO doped solution exhibited a significant increase (130%) in dye photostability (half-life) compared to the undoped solution. The NaN_3 doped solution also showed similar photostability enhancement. This is consistent with results from an assessment of the photostability of PM-567 in methanol and ethanol solutions containing NaN_3 and DABCO, using stimulated emission (conversion efficiency) measurements [7,8]. In the present study, a nominal (23%) increase in PM-567 photostability was observed for solutions containing *n*-propyl gallate. The singlet oxygen quenching rates for NaN_3 and DABCO are 2.3×10^8 l mol^{-1} s^{-1} and 5.4×10^8 l mol^{-1} s^{-1}, respectively [12]. In our experiments, the high ratios of antioxidant to dye concentrations prevent this difference in quenching rates from translating to a difference in the relative photostability enhancement for DABCO versus NaN_3. The high quenching rate constants for NaN_3 and DABCO may be attributed to rapid complex formation in which electron(s) are donated from the quencher to $^1O_2$. The lower photostability enhancement of *n*-propyl gallate may be attributed to a combination of two factors. First, the *n*-propyl gallate singlet oxygen quenching rate constant could be lower, perhaps due to hydrogen abstraction

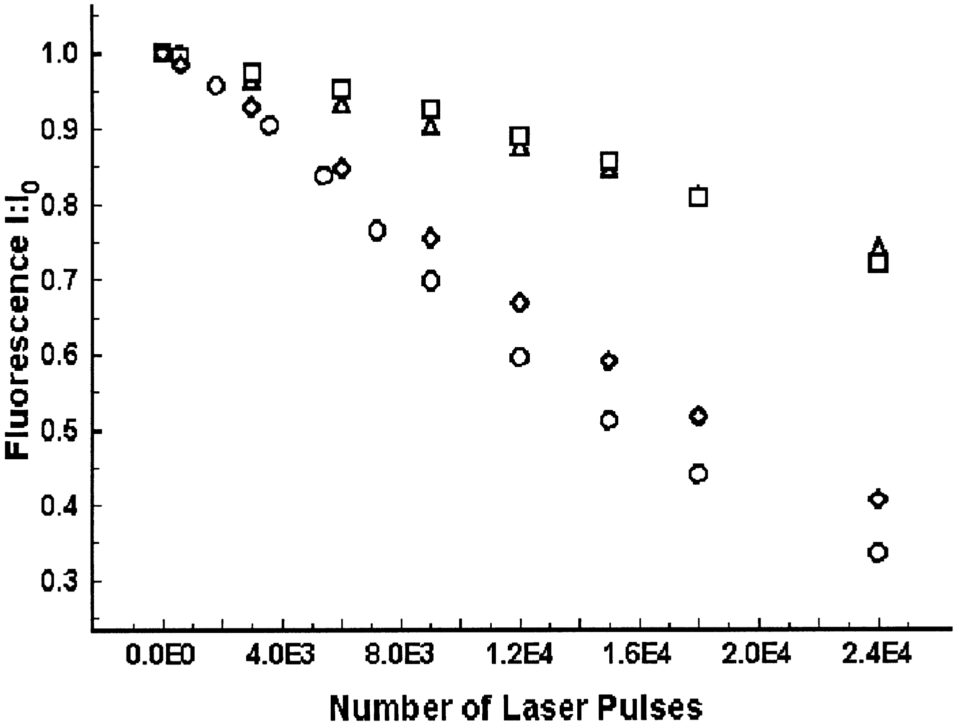

Fig. 1. The decrease in normalized fluorescence with accumulated laser pulses for PM-567/methanol solutions containing various antioxidants: O$_1$ no antioxidant, Δ DABCO, □ NaN_3, and ◇*n*-propyl gallate.

rather than rapid complex formation, although presently, the singlet oxygen quenching rate of *n*-propyl gallate is unknown. Secondly, even if the quenching rate constants were equal for all antioxidants in this study, the degree of physical vs. chemical quenching could vary. Azide ion is known to be a physical quencher, but the relative proportions of physical versus chemical quenching for DABCO and *n*-propyl gallate are unknown. The lower photostability of PM-567 in the presence of *n*-propyl gallate could be attributed to a greater degree of chemical (reactive) quenching than physical. Chemical quenching would reduce the amount of antioxidant as a function of accumulated laser pulses, so that quenching becomes less efficient. These observations point out the need for data such as singlet oxygen quenching rate constants for antioxidants in a variety of solvents and the proportion of physical versus chemical quenching associated with those antioxidants.

A singlet oxygen quenching experiment was conducted on a 4.5×10^{-5} M PM-567/ethanol solution containing diphenyl isobenzofuran (DPBF) at a 10:1 DPBF:dye mole ratio. While the singlet oxygen-quenching rate of DPBF is known to be 30 times that of PM-567 [6], the results in Fig. 2 show a decrease in dye photostability in the presence of DPBF. This could be attributed to the direct interaction between DPBF and the excited dye. Another possible explanation is that the small, but nonzero DPBF absorbance at 532 nm could lead to DPBF sensitized singlet oxygen production and subsequent degradation of the dye via Eqs. (1)–(6). Thus, when evaluating antioxidant-based dye photostabilizers, factors in addition to the relative singlet oxygen-quenching rate must also be considered.

3.2. Concentration dependence

Over the 6×10^{-5}–5×10^{-4} M concentration range, the photostability of PM-567 was essentially concentration independent, with only a small enhancement at lower concentrations (Fig. 3).

The decrease in photoluminescence as a function of accumulated laser pulses follows first-order kinetics at these low concentrations. By utilizing the reaction mechanism illustrated in Eqs. (1)–(8), and by making the steady state approximation for all intermediates ([$^1O_2$], [$^1D^*$], and [^3D]), the rate expression Eq. (9) is obtained for the dye (^1D).

$$\frac{d[D]}{dt} = -\frac{k_5k_3k_1[D]^2}{(k_2+k_3)\{(k_5+k_6)[D]+k_Q[Q]+k_7\}} \tag{9}$$

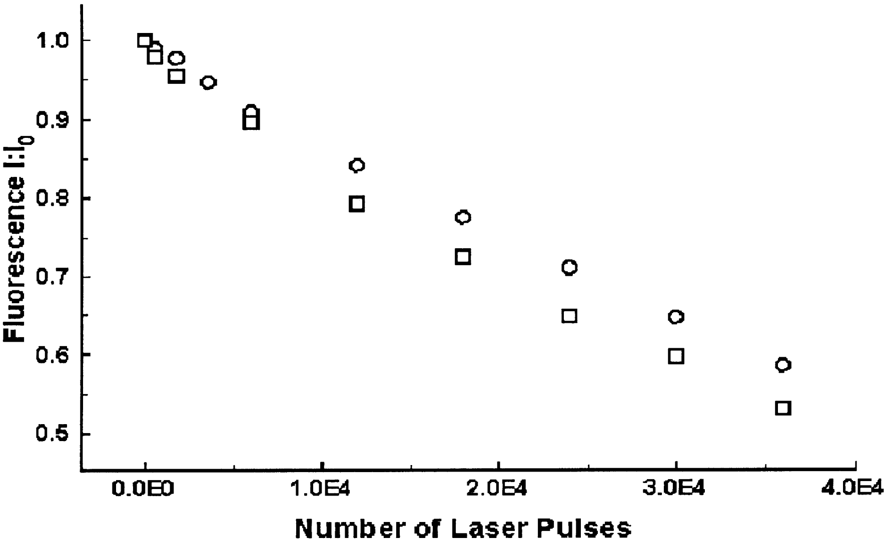

Fig. 2. The decrease in normalized fluorescence with accumulated laser pulses for PM-567/ethanol solutions with (□) and without (○) DPBF.

However, $(k_5+k_6)[\mathrm{D}]+k_q[\mathrm{Q}] << k_7$ [6,13]$_1$ so this simplifies to Eq. (10),

$$\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t}=-\frac{k_5k_3k_1}{k_7}[\mathrm{D}]^2 \tag{10}$$

which is inconsistent with the observed first order kinetics. At low concentrations, there is preference for the dye to react with the particular $^1O_2$ that it generated, producing a geminate-reaction [14]. This would lead to the dye–$^1O_2$ complex undergoing a photooxidation reaction.

To convert the homogeneous photooxidation model above into the heterogeneous geminate photooxidation, model steps (4)–(6) are replaced by steps (11)–(16).

$$^3\mathrm{D}+{}^3\mathrm{O}_2 \underset{k_{-\mathrm{d}}}{\overset{k_\mathrm{d}}{\rightleftarrows}} \left({}^3\mathrm{D}+{}^3\mathrm{O}_2\right) \tag{11}$$

$$\left({}^3\mathrm{D}+{}^3\mathrm{O}_2\right) \xrightarrow{k_\mathrm{f}} \left(\mathrm{D}+{}^1\mathrm{O}_2\right) \tag{12}$$

$$\left(\mathrm{D}+{}^1\mathrm{O}_2\right) \xrightarrow{k'_{13}} \mathrm{DO_2(oxidized\ product)} \tag{13}$$

$$\xrightarrow{k'_{14}} \left(\mathrm{D}+{}^3\mathrm{O}_2\right)$$

Physical quenching by dye and solvent (14)

$$\xrightarrow{k_{15}} \mathrm{D}+{}^1\mathrm{O}_2 \tag{15}$$

$$\left(\mathrm{D}+{}^1\mathrm{O}_2\right)+\mathrm{Q} \xrightarrow{k'_Q} \left(\mathrm{D}+{}^3\mathrm{O}_2\right)+\mathrm{Q} \tag{16}$$

Invoking the steady state approximation for all intermediates leads to a first order rate expression for dye photooxidation [Eq. (17)].

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{DO}_2]}{\mathrm{d}t}&=-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t}=k_{13}\left[\left(\mathrm{D}+{}^1\mathrm{O}_2\right)\right]\\&=\frac{k_{13}k_1k_3}{\left(k_{13}+k_{14}+k'_8+k'_\mathrm{Q}[\mathrm{Q}]\right)(k_2+k_3)}[\mathrm{D}]\end{aligned} \tag{17}$$

Integration of Eq. (17) leads to Eq. (18):

$$[\mathrm{D}]=[\mathrm{D}]_0\exp[-k_{h\nu}t] \tag{18}$$

where $k_{h\nu}=\frac{k_{13}k_1k_3}{\left(k_{13}+k_{14}+k_{15}+k'_\mathrm{Q}[\mathrm{Q}]\right)(k_2+k_3)}$ a rate constant proportional to laser fluence.

Eq. (17) does not explicitly account for the slight concentration dependence of $k_{h\nu}$ apparent in Fig. 3, which shows a high $k_{h\nu}$ for low dye concentrations. The concentration dependence of $k_{h\nu}$ is a manifestation of the *filter effect,* in which incident radiation is attenuated in the bulk of the

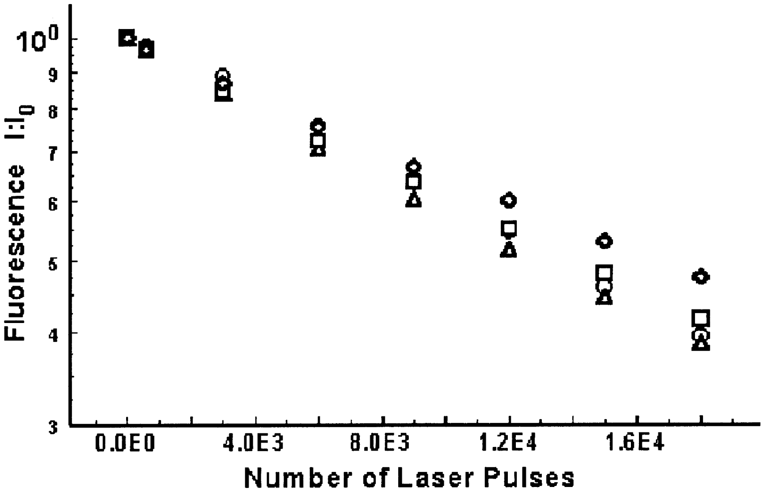

Fig. 3. The concentration dependence of PM-567 photostability in methanol. O 5.00×10^{-4} M, Δ 2.50×10^{-4} M, □ 1.25×10^{-4} M, and ◇ 6.25×10^{-5} M.

sample matrix [15]. Higher dye concentrations lead to greater attenuation of laser light penetrating the bulk of the sample resulting in lower $k_{h\nu}$ values.

The ability to reliably compare the photostability of dye solutions of varying concentrations requires deriving an expression that corrects (normalizes) for concentration dependent filter effects. In this regard, a *normalized photostability* quantity has been reported [7,8], which equals the half-life computed for the *normalized input energy*.

$$N_{\mathrm{IE}} = \text{normalized input energy} = \frac{Pt}{[\mathrm{D}]_0 V} \qquad (19)$$

where P = power (laser power), t = time of irradiation, V = volume.

$$[\mathrm{D}] = [\mathrm{D}]_0 \exp\left(\frac{k_{L\nu} V[\mathrm{D}]_0}{P} N_{\mathrm{IE}}\right) \qquad (20)$$

$$\ln\frac{[\mathrm{D}]}{[\mathrm{D}]_0} = -k_{h\nu}\frac{V}{P}[\mathrm{D}]_0 N_{\mathrm{IE}} = kN_{\mathrm{IE}} \qquad (21)$$

Since $k' = k_{h\nu}V/P[\mathrm{D}]_0$, the apparent rate constant is proportional to $[\mathrm{D}]_0$, plotting $\ln I/I_0$ vs N_{IE} yields slopes ($-k'$) proportional to $[\mathrm{D}]_0$. The apparent photodegradation rate constants obtained from data in Fig. 4 are proportional to initial dye concentration. Thus the *normalized photostability* seems to overcompensate for the filter-effect concentration dependence (Table 1).

When we attempted to measure the effects of antioxidant addition on the photostability of 532 nm-irradiated PM-567/PMMA thin films via observation of fluorescence, it was not possible to detect any difference in the rate of photoluminescence decrease with accumulated laser pulses. These experiments utilized PM-567/PMMA films containing varying amounts of DABCO or *n*-propyl gallate. This contrast in previously reported results [8] could be due to the large difference in bulk: surface area ratio for our 1 μm films and the 1 cm thick solid state dye lasers. In the case of thin films, dye photodegradation may be dominated by singlet oxygen that is active at the sample surface, where oxygen molecules need not diffuse far. This would reduce the number of dye interactions with antioxidants in the excited state, as dye molecules on the film surface are not completely surrounded by antioxidant molecules. In addition, it is possible that the observed difference arises from the fact that our PM-567/PMMA films were prepared by spin casting solutions made by dissolving PM-567, DABCO and PMMA in a common solvent, followed by vacuum heating to remove the solvent. The previous substrates were prepared by casting solutions of PM-567 and DABCO dissolved in

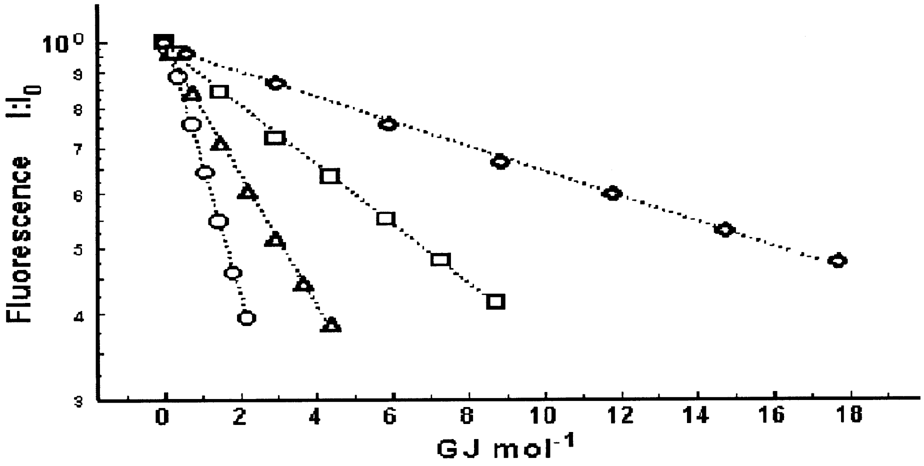

Fig. 4. Fluorescence vs. normalized input energy for varying concentrations of PM567 in methanol. ○ 5.00×10^{-4} M, Δ 2.50×10^{-4} M, □ 1.25×10^{-4} M, and ◇ 6.25×10^{-5} M, - - - - = least squares fit to $\ln\frac{[\mathrm{D}]}{[\mathrm{D}]_0} = k'N_{\mathrm{IE}}$ for each concentration.

Table 1
Normalized photostability rate constants, k', obtained from least squares fit of Eq. (21) to each concentration

PM-567/methanol concentration (M)	K' (mol GJ^{-1})	$k' \div$ concentration
5.00×10^{-4}	0.44	880
2.50×10^{-4}	0.22	880
1.25×10^{-4}	0.10	800
6.25×10^{-5}	0.04	640

methyl methacrylate monomer [8]. This could result in a difference in the number of singlet oxygen traps. An investigation of PM-567/PMMA photostability at varying film thicknesses, dye and antioxidant concentrations, and film formation from colored monomers is in progress.

4. Conclusions

The photostability of methanol solutions of pyrromethene 567 laser dye has been determined by measuring the decrease in photoluminescence as a function of accumulated 532 nm laser pulses. A dramatic photostability enhancement occurs following the addition of DABCO or NaN_3, whereas only a nominal enhancement occurs following the addition of *n*-propyl gallate. Our results also point to a need to determine the physical and chemical quenching rate constants for various antioxidants in different solvents. The photodegradation profiles of antioxidant-free solutions were fit by a single exponential in accordance with a heterogeneous dye–singlet oxygen geminate reaction process. A weak correlation between dye concentration and the first-order photodegradation of PM567 in methanol suggest that the concentration dependence cannot be adequately accounted for by normalized photostability. Preliminary studies on the photostability of PM-567/PMMA solid films suggest that DABCO addition does not affect photostability.

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