

Photodegradation Kinetics of Methyl Salicylate in Poly(methyl Methacrylate)

CLIFFORD L. RENSCHLER,* *Sandia National Laboratories,
Albuquerque, New Mexico 87185*

Synopsis

It has been found that methyl salicylate (MS) undergoes a photoinduced decarboxylation to form phenol with a quantum yield of ca. 8×10^{-5} . The reaction is first order and the rate constant is proportional to the irradiance used. An activation energy of 1.2 kcal/mol was determined. Computer simulations were used to predict whether sufficient UV screening would be provided by MS-containing PMMA lenses over the projected lifetime of solar photovoltaic devices. An effective screening lifetime of less than 2 years is predicted.

INTRODUCTION

A number of compounds are commonly introduced into polymer formulations to act as stabilizers against the deleterious effects of exposure to UV light.¹⁻⁴ The protective mechanism can be due to a shielding effect and/or a quenching effect.² With shielding, the polymer is exposed to fewer UV photons because most of these photons are absorbed by the stabilizer. Of course, the stabilizer itself should be UV stable so that the absorbed light is simply thermalized. The quenching mechanism provides another deactivation route for polymer excited states, which lowers the quantum yield of the photodegradation reaction.

Obviously, photostabilization by the shielding mechanism protects not only the polymer from UV exposure, but any material underneath the polymer as well. This has obvious advantages in solar concentrator applications. For the system of interest here, a poly(methyl methacrylate) (PMMA) lens was being considered for use in a solar concentrator with the concentrated light flux to be projected on a silicon photocell assembly. The assembly included organic coated electrical connections and other organic materials which could not tolerate long-term exposure to UV light. It was found that methylsalicylate (MS) had been added to the PMMA. While the MS was probably not added as a photostabilizer, it nevertheless provided UV screening for the photocell.

MS absorbs over the approximate wavelength range 260–340 nm, with a maximum absorbance in PMMA at 306 nm, where absorbance is defined as $-\log(\text{transmittance})$. From the absorbance spectra of thin films of this material, it was calculated that a 2 mm thick sheet would have an absorbance >9 at 306 nm, providing nearly total UV screening protection against photons near this wavelength. However, under simulated solar irradiation,

* This work performed for the U. S. Department of Energy under Contract DE-AC04-76DP00789.

the concentration of MS was observed to fall off. Therefore, it was of interest to study the photoloss process and to determine its rate under a variety of conditions to predict whether adequate UV screening would be provided over the expected lifetime of the solar cell assembly (up to 20 years).

Thin films of the MS-containing PMMA were cast on quartz plates and the MS absorbance monitored with light exposure at different temperatures and different irradiance levels. From these data the reaction order, activation energy, and rate dependence on irradiance were determined. Computer simulations were then used to predict length of time over which adequate screening protection would be provided.

The experimental techniques and simulations outlined here should be broadly applicable to the study of absorber photoloss from polymeric matrices.

EXPERIMENTAL

The PMMA lens was obtained from E-Systems Inc. (Garland, Tex.) and cut into small chips. A number of these chips were weighed and dissolved in reagent grade methylene chloride (Spectrum Chemical Mfg. Corp., Redondo Beach, Calif.) at a concentration of 4 w/v%. PMMA films were cast on quartz plates which were 1 in.² and either 1 or 2 mm thick. The casting process involved placing a plate on the bottom of a 100-mL beaker and covering it with ca. 3.4 mL of the methylene chloride solution. The beaker was then covered with an inverted funnel with glass wool in the funnel stem and beaker lip to insure slow solvent evaporation. As the solvent receded below the plate surface, a film was deposited. After removing it from the beaker, the sides and bottom of the plate were cleaned of any PMMA which might have adhered.

Film-bearing plates were irradiated by an Oriel 1000 W Xe lamp, whose output was passed through a collimating lens and two 0.125 in. thick plates of Pyrex glass. The resulting spectral distribution mimicked quite closely the true solar spectrum at air mass 1, as shown in Figure 1,⁵ where air mass 1 is the atmosphere through which solar radiation must pass from a point directly overhead to reach sea level. The light beam fell on a copper platen which could be moved closer or further from the lamp along an optical rail. The platen contained a thermostated heating system which allowed for the maintenance of elevated temperatures to a tolerance of ca. $\pm 1^\circ\text{C}$. Plates were mounted on the platen using a thin layer of Echotherm 7 thermal grease (Emerson and Cuming, Dewey and Almy Chem. Div., Northbrook, IL) to promote good thermal contact. A reflectance spectrum was taken to insure that reflection off the thermal grease was not contributing to the total irradiance seen by the film. The reflectivity of the grease was found to be only 4.5% in the wavelength range of MS absorbance (< 360 nm).

The irradiance was measured at various points along the optical rail using a Gamma Scientific Radiometer (DG85L Spectral Scanning System, NM 9H double monochromator, D-46AOPM tube system, DR-2 digital radiometer, SC-5 digital controller, and GS-5150 deuterium lamp).

Absorbance measurements were taken with a Cary 17 Spectrophotometer. Fluorescence measurements were taken using a laboratory-built fluori-

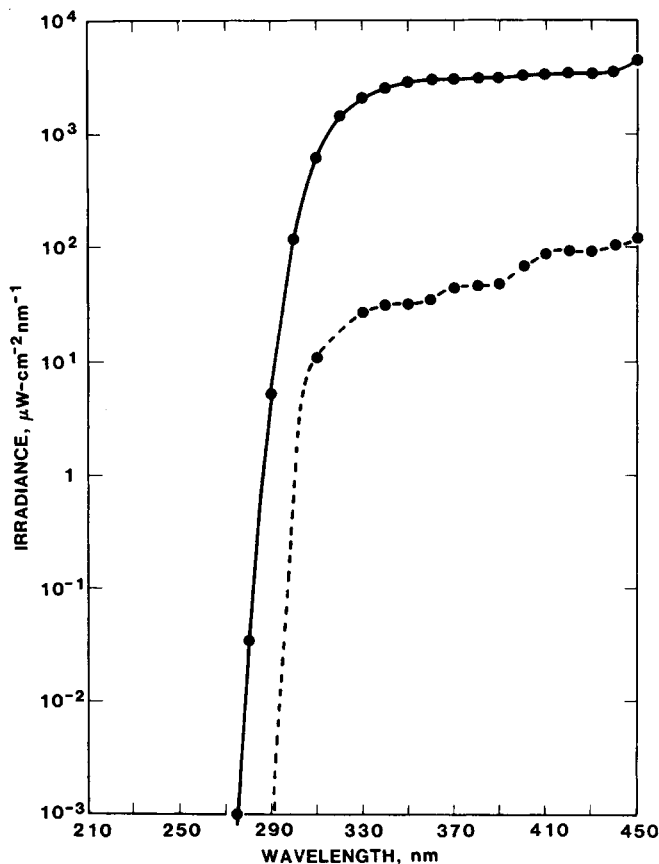


Fig. 1. Irradiance versus wavelength: (—) solar simulator used in present study; (- - -) typical solar spectrum (taken at Gainesville, Fla. and reported in *Opt. Rad. News*, No. 3, NBS publication, Oct. 1981).

meter employing an Hanovia 200 W Hg-Xe lamp and an excitation grating monochromator with $f/4$ collection optics. Right angle detection was employed through a Spex 1702 Grating Emission Monochromator and an RCA 3104 Photomultiplier Tube.

Mass spectral data were taken with a Finnigan MAT 1125 Mass Spectrometer with a 6 ft \times 0.125 in. column, with 3% SP2100 liquid phase on 80/100 Supelcoport at 130°C isothermal, 30 mL/min He carrier gas.

Film thickness measurements were taken with a Tencor Alpha Step diamond scribe. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-2.

Reagent grade ethanol was obtained from AAPER Alcohol and Chemical Co. (Louisville, KY) and reagent grade cyclohexane was obtained from Spectrum Chemical Co., both used as received.

RESULTS AND DISCUSSION

The photoscreening agent found in the PMMA of interest was determined to be MS by GC-mass spectral analysis after extraction into ethanol. The

identification was confirmed by comparison of absorbance spectra of the extract with that of pure MS in ethanol.

The rate of loss of MS from the PMMA films was monitored by taking an absorption spectrum of a PMMA film, irradiating the film for a specific period of time, and then taking another spectrum of the same film to observe the decrease in MS absorbance. Typical absorbance spectra for a PMMA film, both before and after irradiation, are shown in Figure 2. The percentage decrease in absorbance was measured for each film at the wavelength of maximum absorbance, 306 nm. A tradeoff was necessary in the choice of film thickness to achieve an appropriate MS absorbance. A film which was too thin would give an absorbance too low to be monitored with any degree of precision. Conversely, a thick film would produce an absorbance large enough to affect a significant gradient in irradiance across the depth of the film. A maximum MS absorbance between 0.09 and 0.12 was chosen as a suitable range. The average irradiance seen over the depth of a film of thickness t at a given wavelength can be given by

$$\overline{F(x)} = \frac{\int_0^t F(x) dx}{\int_0^t dx} = \frac{\int_0^t 10^{-\epsilon x} dx}{\int_0^t dx} = \frac{1 - 10^{-\epsilon t}}{\epsilon t (\ln 10)} \quad (1)$$

where $F(x)$ is the irradiance as a function of depth into the film, ϵ is the extinction coefficient at the wavelength of interest, and c is the concentration of absorber. For an (ϵt) value of 0.12, the average value of F across the film's depth will be within 13% of the value at the film's front face. Since most of the light absorption by MS occurs at wavelengths other than 306 nm and with lower extinction coefficients (*vide infra*), the average

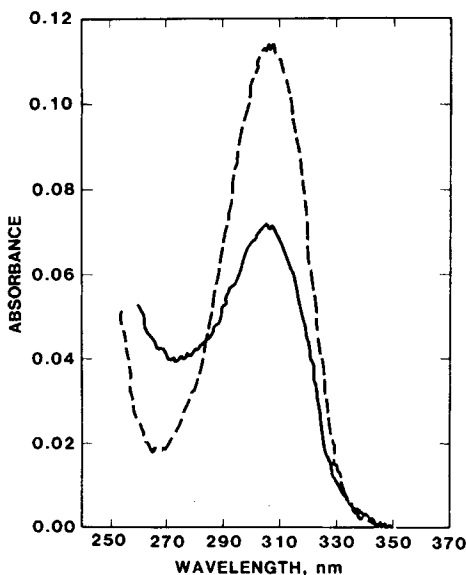


Fig. 2. Absorbance spectra of PMMA film: (---) before irradiation; (—) after irradiation.

irradiance integrated over all wavelengths will likely be within 10% of the irradiance at the front face. This error is probably smaller than the variation in light intensity as emitted by the lamp.

The rapidly increasing absorbance seen in Figure 2 at wavelengths below ca. 260 nm is due to the PMMA film itself. To correct for any absorbance due to PMMA at 306 nm, films of pure PMMA were cast and their absorbance spectra taken. It was found that at 306 nm only a 0.002 absorbance correction need be made to account for PMMA absorbance in films of the thickness used in this study (ca 0.8 mil or 20 μm). This correction was applied to all data presented here. The photoproduct formed upon irradiation was found to be phenol (*vide infra*). Since the ratio of the MS extinction coefficient to that of phenol at 306 nm is > 100 ,⁶ no correction was applied for the growth of phenol absorbance with irradiation.

The product of the MS extinction coefficient at 306 nm and the MS concentration in PMMA, ϵc , was measured in two ways. With the first method, the density of the PMMA was measured to be 1.19 g/cm³ using a calcium nitrate density gradient column. By dissolving a known weight of PMMA in 100 mL of methylene chloride, the change of MS concentration upon dilution could be calculated. From the absorbance of a 1 cm path length cell (and after correction for PMMA absorbance), the ϵc product in the original PMMA was determined to be 46.4 cm⁻¹.

The more direct method of measuring both the absorbance and the thickness of a film yielded an ϵc value of 54 cm⁻¹. The two determinations agree within ca. 15%, and the difference is probably due to the error in a diamond scribe thickness determination of a relatively soft (i.e., polymeric) material like PMMA.

The MS concentration in PMMA was determined by measuring the ϵ_{max} of MS in cyclohexane. The value of 4400 M⁻¹ cm⁻¹ gives a concentration of 10.5 mM.

Kinetic Order

To determine the kinetic order of the photodegradation process, a number of films were irradiated at 60°C and an irradiance of 5040 $\mu\text{W} \cdot \text{cm}^{-2}$ for different lengths of time. (This value is the integrated spectral irradiance taken over the range 280–340 nm. All references to irradiance given in this paper were determined in this way, except the entries in Table I, which are given for specific wavelengths.) This corresponds to a solar irradiance of 6.3 suns, or 6.3 times the solar irradiance at air mass 1. A plot of $\ln c$ vs. time, where c is the concentration of MS remaining after irradiation expressed as a percentage of the concentration prior to irradiation, is shown in Figure 3. A straight line is obtained, indicating a first-order kinetic process. The 120-h data point was taken to unambiguously distinguish between a first-order and a zeroth-order process, which appear similar at low loss levels. In order to insure that the process was not a bimolecular reaction with oxygen which appeared pseudo first order, a solution phase reaction was carried out in the absence of oxygen. An absorbance spectrum was taken of a dilute solution of MS in cyclohexane. The solution was placed in a quartz tube and put through three freeze-pump-thaw cycles to exclude

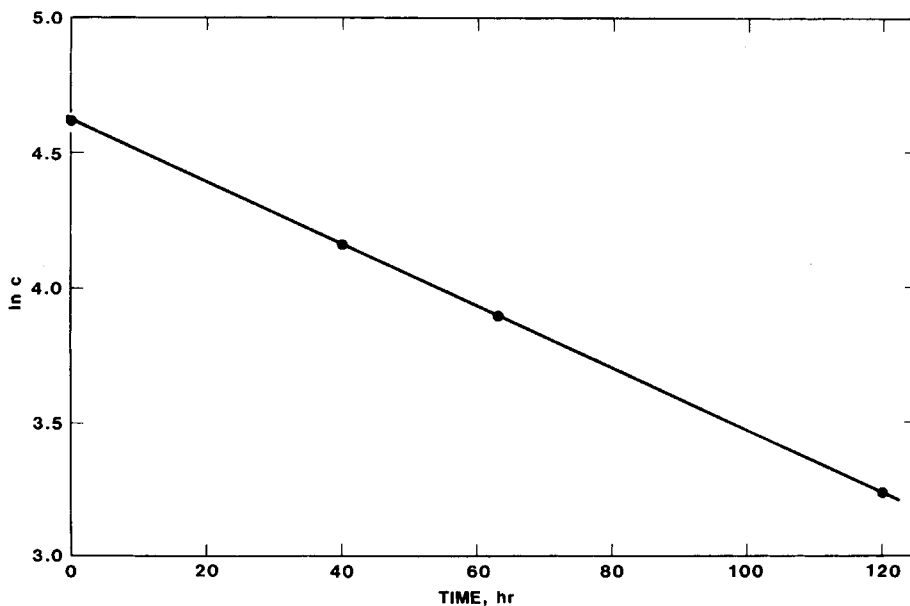


Fig. 3. Natural log of MS concentration c vs. irradiation time at 6.3 suns and 60°C.

oxygen. The tube was then sealed *in vacuo* and irradiated at $5450 \mu\text{w} \cdot \text{cm}^{-2}$ (6.8 suns) for ca. 450 h. When the tube was broken, it was found that the solution had remained under vacuum. A new absorbance spectrum revealed that the MS concentration had dropped to <10% of its original value. Clearly, oxygen does not participate in the photodegradation reaction.

Dependence on Irradiance

The dependence of the rate constant k on irradiance was determined by averaging several single point rate determinations at different irradiance levels and at 60°C. The light source was not perfectly collimated, so the irradiance on the sample could be varied by moving the platen along the optical rail. The rate constants defined here are not absolute, i.e., they are not constants for a population of MS molecules in the excited state. Rather, they define the rate of reaction for the entire population of MS molecules and are dependent on the steady-state fraction of molecules in the excited state. As seen in Figure 4, the rate constant was found to be directly proportional to irradiance. The line drawn is the linear least squares line with forced zero intercept. The slope of the line is $1.5 \times 10^{-3} \text{ h}^{-1} \text{ sun}^{-1}$, where 1.0 sun is equivalent to $797 \mu\text{w cm}^{-2}$ over the 280–340 nm range. One might expect such a proportionality for a system in which the irradiance gradient through the sample is small and the light level is not high enough to saturate the MS excited states. The maximum irradiance obtained here was ca. $5190 \mu\text{w cm}^{-2}$; this corresponds to 6.5 suns or $1.45 \times 10^{-8} \text{ einsteins cm}^{-2} \text{ s}^{-1}$, which is not extremely high.

Temperature Dependence

The temperature dependence on the rate constant was determined at an irradiance of $5500 \mu\text{w cm}^{-2}$ (6.9 suns) at 60, 80, and 90°C. This represents

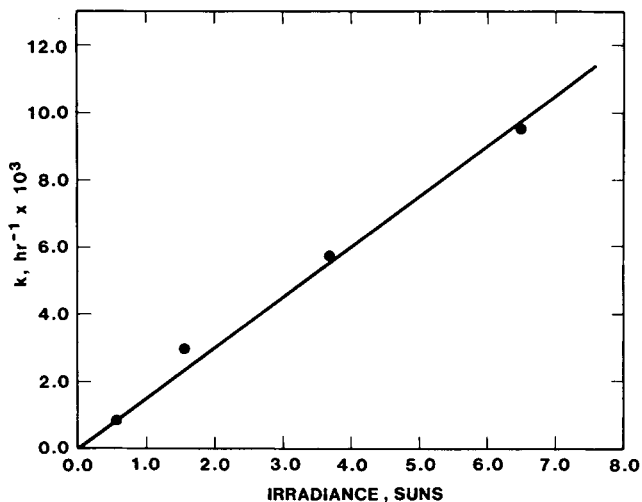


Fig. 4. Rate constant for photolysis k vs. irradiance at 60°C.

a somewhat restricted temperature range. Lower temperatures require active cooling of the platen, which results in wider temperature variations during the course of the experiment. DSC measurements on samples of the PMMA showed its glass transition temperature T_g to be between 93.3°C and 94.3°C. Irradiation at temperatures above T_g was avoided since it might cause sample deformation. An Arrhenius plot of these temperature data is shown in Figure 5. The slope of -600 K yields an activation energy E_a of only 1.2 kcal/mol. This indicates a very small temperature dependence on the reaction rate. From the above data, the rate constant at 40°C (ambient temperature for the solar assembly) and 1.0 sun was determined to be $1.3 \times 10^{-3} \text{ h}^{-1}$.

In order to establish that the photolysis was due to a chemical reaction

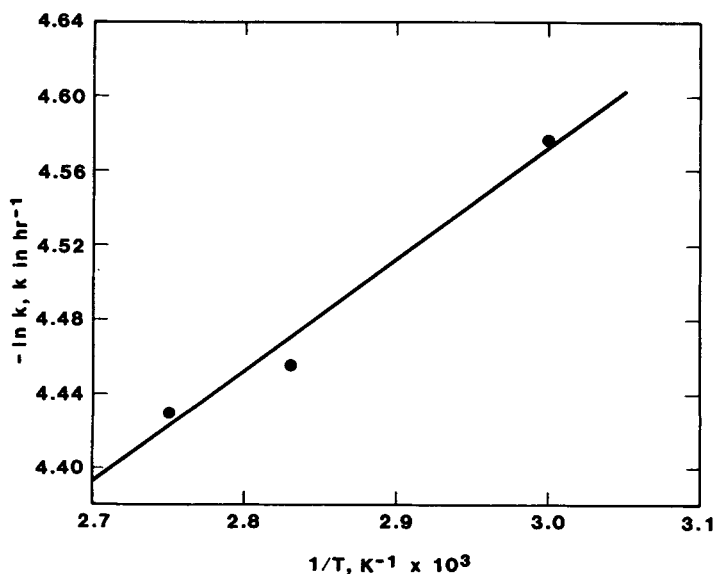


Fig. 5. Arrhenius plot, $\ln k$ vs. $1/T$.

and not a volatilization, a film was affixed to the platen for 23.5 h at 80°C with the sample in the dark. Under the same conditions with a 6.9 sun flux the MS concentration would be expected to drop ca. 25%. In the absence of light, however, no decrease in MS concentration was observed. Clearly, the MS loss is due to a light-driven reaction rather than a volatilization. This is consistent with the small temperature dependence of the process. Of course, volatilization of the MS might be observed on a longer time scale, as a number of low molecular weight salicylates are known to be subject to volatilization from polymer formulations.³

Identification of Photoproduct

It was somewhat surprising to find MS as an additive in the PMMA formulation, although a number of phenyl esters of salicylic acid are commonly used as UV stabilizers. These include the phenyl, *p*-*tert*-octylphenyl, and *p*-*tert*-butylphenyl esters.^{3,7} These compounds undergo a reaction thought to be a photoinduced Fries rearrangement to yield dihydroxybenzophenones.^{3,8,9} Such a rearrangement can only occur with phenolic esters, so another mechanism must be operative with MS. The photochemistry of MS has been extensively studied,¹⁰⁻¹⁵ but is not completely understood. It is believed that an excited state proton transfer from the phenolic oxygen to the carbonyl oxygen results in tautomeric forms and a dual fluorescence. It has also been proposed that there exists a fast radiationless decay route of unknown mechanism.¹⁴ In any case, MS has been considered stable toward the irreversible formation of photoproducts. Apparently, the photodegradation reported here has not been previously observed.

The photoproduct formed in these experiments did not absorb strongly at 306 nm or longer wavelengths. The absorbance of the irradiated films is greater than the absorbance before irradiation at wavelengths below ca. 283 nm, although slight variations in this wavelength from one film to the next will not allow one to state conclusively that 283 nm is a true isosbestic point. The most likely photoproduct which would absorb below 283 nm is phenol, which could result from the photodecarboxylation of MS. This was confirmed by the irradiation of solutions of MS in ethanol. Figure 6 shows the fluorescence emission spectra of a $3.07 \times 10^{-5}M$ solution of MS both before and after irradiation at ca. 6.5 suns for 94 h. The dual fluorescence of MS (at ca. 350 nm and 450 nm) was observed and after irradiation a shorter wavelength band was seen to grow in. The new band matched well the fluorescence of pure phenol shown on the same graph. The peak at 288 nm was an Hg peak from the lamp spectrum. A small apparent redshift of the phenol band in the irradiated solution was due to the overlap of the MS fluorescence. The improvement in the signal-to-noise ratio for the MS bands after irradiation was due to energy transfer from the phenol, which absorbs the 265 nm excitation beam much more strongly than MS. Other potential photoproducts, such as benzene and benzoic acid, do not produce fluorescence spectra which match as closely the spectrum of the irradiated solution.

More conclusive evidence for phenol formation was provided by GC-mass spectrometry. A solution of MS in ethanol (ca. 25% by volume) was irradiated at ca. 6.5 suns for 52.5 h. The irradiation was done in a microcuvette

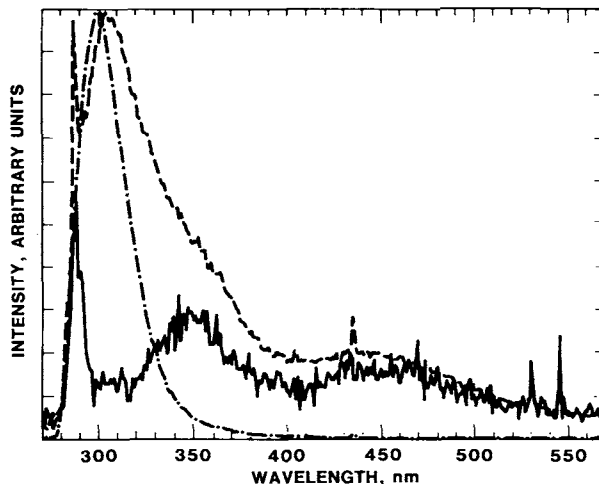


Fig. 6. Fluorescence spectra: (—) MS; (- - -) phenol; (- · -) MS after 94 h irradiation at 6.5 suns.

(1 mm path length), which was sealed with Teflon stoppers to slow evaporation. By using single ion detection at mass 94 to increase sensitivity, a product with the proper mass and the same retention time as phenol was observed to be present after irradiation. Pure MS and ethanol were also checked to insure that neither was the source of phenol.

Reaction Quantum Yield

The wavelength dependence of both the absorbance of a typical film and the irradiance incident on it are given in Table I. The maximum absorbance (at 306 nm) is 0.100 and the total irradiance is 5.8 suns. One can determine from these data that an irradiance of 1.0 sun is equivalent to 1.33×10^{15} photon $\text{cm}^{-2} \text{s}^{-1}$. Integrating the absorbed irradiance over the absorption band gives a fraction of absorbed photons of 4.8%, equal to 6.4×10^{13} photon $\text{cm}^{-2} \text{s}^{-1}$. By using the rate constant for photodegradation at 1.0 sun and 40°C of $1.3 \times 10^{-3} \text{ h}^{-1}$, the same film would lose 5.1×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$ to photodegradation. This means the quantum yield for the photodegradation ϕ is only 8×10^{-5} . Since the photoreaction is such an inefficient process, it is not surprising that it has not been previously observed. The low ϕ value also explains the difficulty of producing an observable concentration of photoproduct.

As stated above, the rate constants quoted here are not absolute. One way to determine an absolute rate constant would be to saturate the excited states using an extremely intense light source. Alternatively, if enough information is known about the dynamics of competing processes, such as fluorescence, a ratioing technique can be used to find the absolute rate constant.

The fluorescence quantum yield ϕ_F of the 450 nm emission band of MS in a solid matrix (octadecane) has been reported as 0.038 with a radiative rate constant of $1.2 \times 10^8 \text{ s}^{-1}$.^{14,15} If one assumes that ϕ_F for MS in octadecane is the same as in PMMA and that the two emission bands have approxi-

TABLE I
Wavelength Dependence of Absorbance and Irradiance of a Typical Film

Wavelength (nm)	Source irradiance I ($\mu\text{J}/\text{s cm}^2 \text{ nm}$)	Source irradiance (photons/s $\text{cm}^2 \text{ nm}$)	Film absorbance	Light absorbed $I \times (1 - T)^a$ ($\mu\text{J}/\text{s cm}^2 \text{ nm}$)
306	10.1	0.155	0.100	2.1
308	16.5	0.256		
310	20.9	0.326	0.0974	4.2
312	33.0	0.518		
314	45.6	0.720	0.0877	8.3
316	59.9	0.952		
318	69.6	1.11	0.0737	10.9
320	83.9	1.35		
322	97.9	1.58	0.0509	10.8
324	123	2.00		
326	134	2.20	0.0298	8.9
328	164	2.70		
330	190	3.15	0.0138	5.9
332	208	3.47		
334	237	3.98	0.00474	2.6
336	256	4.32		
338	278	4.72		
340	299	5.11	0.00175	1.2

^a T is transmittance.

mately the same lifetime, then the ratios of the quantum yields for fluorescence and photodegradation should equal the ratio of their rates. This gives an absolute rate constant for the photoreaction of $2.5 \times 10^5 \text{ s}^{-1}$ ($9.0 \times 10^8 \text{ h}^{-1}$) and a steady state fraction of MS molecules in the excited state at 1.0 sun of 1.5×10^{-12} . The second assumption given above has been shown not to be completely justified, as the lifetime in acetonitrile of the form emitting at 340 nm is about a factor of 10 greater than the lifetime of the species emitting at 450 nm.¹⁵ Nevertheless, it seems clear that the maximum irradiance obtainable with this lamp will not saturate the MS excited states. This fact, together with the use of optically dilute films, is consistent with the direct proportionality of irradiance and reaction rate.

Simulation of Photoloss from Thick Sheets

As mentioned above, the rate of loss of MS from thick (highly absorbing) sheets of PMMA needs to be known to determine the useful shielding lifetime of MS in a particular application. In highly absorbing sheets, there is a very severe depth dependence of absorption, which is wavelength-dependent. There are several ways to model such a system, the simplest being to assume a square-wave absorption profile. Under these conditions, the entire photoloss is due to photons absorbed at the wavelength of maximum absorbance or nearby wavelengths with essentially the same extinction coefficient. Since the MS absorption band is essentially Gaussian in shape, the above model deviates somewhat from reality. However, this model has an analytical solution that can be checked against the computer simulation which insures that the computer closely simulates the proposed model.

With the model described above, the rate of loss of MS, as measured by the change in the absorption band, is proportional to the number of photons absorbed:

$$\frac{-dA}{dt} = k\{1 - \exp[-A(\ln 10)]\} \quad (2)$$

where A is the absorbance of the sheet, k is the rate constant, and t is time. Solving the above equation for t yields

$$t = \frac{-A(\ln 10)}{k} - \left(\frac{1}{k}\right) \ln\{1 - \exp[-A(\ln 10)]\} \quad (3)$$

or

$$t_1 - t_0 = \frac{(\ln 10)(A_0 - A_1)}{k} - \left(\frac{1}{k}\right) \ln\left(\frac{1 - \exp[-A_1(\ln 10)]}{1 - \exp[-A_0(\ln 10)]}\right) \quad (4)$$

A PMMA sheet in the application considered here would be 2 mm thick. Such a sheet would initially have an absorbance at 306 nm of 9.28. The sheet would be considered an adequate screening agent until the absorbance fell below 2.0.

The computer program which simulated the above model divided a PMMA sheet of any thickness into any number of thin slices. After defining the incoming irradiance, the irradiance incident on the front face of each slice was computed along with the loss rate constant (assuming an ambient temperature of 40°C). The concentration of each slice was then adjusted downward with the selected time increment. If the overall absorbance through the slab did not fall below 2.0 after this operation, another time increment was added, and the process was repeated. The number of time increments needed to reach an absorbance of 2.0 was reported.

Using an irradiance of 1.0 sun, a total thickness of 2 mm, 1000 slices, and a 60-h time increment, 212 increments (1.27×10^4 h) produced an absorbance of 1.99. Solving eq. (4) for this change in absorbance predicts that 1.25×10^4 h would be required, which is within ca. 1.5% of the value predicted by simulation. This indicates that the slices modeled have sufficiently low absorbance and the 60-h time increment is sufficiently small to model the mathematical system well. It should be noted that for the A_0 and A_1 values used here, the second term in eq. (4) contributes <0.1% to the total time and can be considered insignificant.

A model which more closely mimics reality, but which is difficult or impossible to solve analytically, would take into account the wavelength dependence of both the irradiance impinging on the PMMA and the MS absorbance. The total number of photons absorbed determines the rate of photolysis. This, in turn, is proportional to the irradiance at each wavelength times the fraction of photons absorbed at that wavelength, all integrated over the absorption band. This product is shown in Table I. Since the ab-

sorbance decreases with increasing wavelength above 306 nm while the irradiance increases in the same wavelength region, the product is greatest at wavelengths near 320 nm. Below 306 nm the irradiance is very low and above 334 nm the absorbance is very low, so only the wavelength range between these limits was considered.

The computer simulation program described above was modified to compute the contribution to MS photoloss at each wavelength from 306 to 334 nm in 4-nm increments. For optically thin samples, the number of photons absorbed at a given wavelength is proportional to the product of the extinction coefficient and the concentration, so that these numbers were computed at each wavelength and used to determine the total rate of MS loss in each slice during each time increment. Since comparison of the computer model with an analytical solution was not possible in this case, the time increment was shortened to 10 h to insure that the decrease in concentration in each slice with each time increment would not be too large. With all other parameters the same as used in the previous simulation, a total time of 4960 h was predicted to reach an absorbance of 2.0. This is considerably shorter than the time predicted by the earlier simulation. The difference is due to the fact that in thick sheets significant absorbance (and therefore significant photoloss) is developed in the long wavelength wing of the absorption band, but this absorbance is not effectively taken into account in the square wave absorption band model.

Of course, the 4960-h screening lifetime at 1.0 suns would translate into different true lifetimes depending on the location of the device, since the average solar irradiance incident on different points of the earth's surface varies widely. However, if one assumes that at a given location, the device would be exposed on average to the equivalent of 8 h/day of a 1.0 sun irradiance, the effective screening lifetime would be ca. 1.7 yr. This is much too short for the UV screening to be useful over the projected life of the device, ca. 20 yr. This will necessitate either protective encapsulation of the solar cell assembly or use of a different screening agent in PMMA.

CONCLUSIONS

Methods were developed to study simulated solar irradiation of thin polymer films. It was found that the MS found in a PMMA lens would photodegrade under this type of exposure. Rate constants were measured under different conditions, and an activation energy and quantum yield determined. These data were then used in computer simulations which predicted that lenses made of this material would not provide effective UV screening over the expected lifetime of solar concentrators.

The author wishes to thank J. E. Cannon for designing and building the solar simulator and for taking much of the kinetic data. Thanks are also due to L. C. Beavis and L. A. Harrah for helpful discussions. The GC-mass spectral analysis of P. J. Rodacy is gratefully acknowledged.

References

1. B. Ranby and J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers*, Wiley, London, 1975.
2. V. Ya. Shlyapintokh and V. I. Gol'denberg, *Eur. Polym. J.*, **10**, 679 (1974).

3. G. C. Newland and J. W. Tamblyn, *J. Appl. Polym. Sci.*, **8**, 1949 (1964).
4. A. Gupta, G. W. Scott, and D. Kliger, *Photodegradation and Photostabilization of Coatings*, ACS Symp. Series 151, American Chemical Society, Washington, D.C., 1981, p. 27.
5. *Optical Radiation News*, Vol. 33, Nat. Bur. Stds. Publ., Washington, D.C., Oct. 1980.
6. I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic, New York, 1971.
7. V. S. Sirokhin and A. A. Efimov, *Khim. Vysok. Ener.*, **14**(2), 139 (1980).
8. J. H. Chandet, G. C. Newland, H. W. Patton, and J. W. Tamblyn, *Soc. Plast. Eng. Trans.*, **1**, 26 (1961).
9. J. C. Anderson and C. B. Reece, *Proc. Chem. Soc.*, 217 (1960).
10. A. Weller, *Naturwissenschaften*, **42**, 175 (1955).
11. A. Weller, *Z. Elektrochem.*, **60**, 1144 (1956).
12. J. Goodman and L. E. Brus, *J. Am. Chem. Soc.*, **100**(24), 7422 (1978).
13. A. U. Acuña, F. Arnat-Guerri, J. Catalán, and F. González-Tablas, *J. Phys. Chem.*, **84**, 629 (1980).
14. A. U. Acuña, J. Catalán, and F. Toribio, *J. Phys. Chem.*, **85**, 241 (1981).
15. K. K. Smith and K. Kaufman, *J. Phys. Chem.*, **82**, 2286 (1978).

Received February 7, 1984

Accepted April 9, 1984