

A SOLID STATE ACTINOMETER BASED ON THE PHOTOREARRANGEMENT OF AZOXYBENZENE IN POLY(METHYL METHACRYLATE)

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Summary

An actinometer system was developed in which a solute (azoxybenzene) was photolysed in a relatively massive block of poly(methyl methacrylate) (PMMA). Pieces which fitted directly into the cuvette holder of a spectrophotometer were cut from sheets of this material. The initially colourless pieces of polymer were photolysed, and the product (*o*-hydroxyazobenzene) was monitored by measuring its absorbance at 420 nm ($\epsilon = 4500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The quantum yield of this photorearrangement had a value of 4.2×10^{-3} , and an empirical relationship allowed the total photon dose incident on any sample to be estimated using a single absorbance measurement. Investigations of other potential solutes revealed that this technique of using PMMA blocks which contain residual monomer is applicable only to photoreactions that do not proceed through free-radical intermediates.

1. Introduction

Solutions of chemical actinometers are the standard systems for measuring the light fluxes in photochemical reactions. Our interest in chemical actinometers lies in the development of systems that are particularly easy to manipulate, and hence that make the technique available to a wider range of researchers. In this paper we describe the development of an actinometer in polymeric solid solution.

Cowell and Pitts [1] first investigated such systems. They used thin films of purified poly(methyl methacrylate) (PMMA) in which was dissolved ("dispersed") the photoactive chemical *o*-nitrobenzaldehyde. The films were typically about 2×10^{-3} cm thick and the progress of the photorearrangement of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid was monitored by IR spectroscopy (a recent application of this technique is described in ref. 2). PMMA is a good medium for such research because it is very transparent to visible and near-UV light.

The advantage of the thin film technique is that highly purified polymer containing no residual monomer can be used. The disadvantage is that not all the incident light is absorbed so that a correction factor must be determined to relate the incident intensity to the absorbed intensity. Furthermore, films this thin are less mechanically rugged than would be desirable. Consequently, we have adopted an alternative approach, namely the preparation of more massive blocks of polymer which are likely to contain unreacted monomer. Under these conditions all the incident radiation can be absorbed.

2. Experimental details

Methyl methacrylate (Fisher), benzophenone (Fisher), *o*-nitrobenzaldehyde (Aldrich) and 1,3-diphenylpropanone (Aldrich) were obtained commercially. Azoxybenzene was prepared by the reduction of nitrobenzene [3] and was crystallized from ethanol (melting point, 34.5 - 36.0 °C). The stabilizer was removed from the methyl methacrylate by washing with aqueous NaOH and water [4].

Solutions of the various photoactive compounds in methyl methacrylate were polymerized in the dark between glass plates using the method of Pinner [4] in which a small amount of benzoyl peroxide is employed as the initiator. After 3 days at 60 °C, rigid transparent sheets were obtained. These were kept in the dark until needed. Rectangular pieces of polymer of dimensions 1.2 cm × 4.0 cm were cut from these sheets and their surfaces were cleaned by rinsing with ethanol. These pieces fitted directly into the cuvette holder of a Varian DMS 90 spectrophotometer. Concentrations of azoxybenzene in PMMA refer to the nominal concentrations of azoxybenzene in the monomer.

The absorption spectra of azoxybenzene and 2-hydroxyazobenzene were obtained in methyl methacrylate solution, and it was assumed that the molar absorptivity was unchanged in PMMA. However, the concentration increases upon polymerization on account of shrinkage (about 30%).

The irradiation apparatus was a Rayonet model RUL photoreactor equipped with eight RUL 3500 lamps having their maximum output at 350 nm. The apparatus was warmed up for 15 min prior to each run. The polymer blocks were irradiated simultaneously using a carousel system to ensure equal light absorption by all samples. Each block was positioned so that its edge was facing the lamps; consequently both the front and rear faces of the block were illuminated equally. This arrangement meant that when the concentration per unit area was calculated the experimental absorbance was divided by 2 prior to normalizing the data per unit area. Samples were handled in diffuse room light and not in a dark-room during the manipulations to measure the absorbance because the azoxybenzene actinometer is rather unreactive to visible light. Unirradiated blocks of solute in polymer were used to set the instrument to zero and to act as the reference. Product formation was monitored at 420 nm ($\epsilon = 4500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

For the actinometry experiments the actinometer was a solution of azoxybenzene (1 mg ml^{-1}) in 95% ethanol [5]. The solutions were irradiated in conventional spectrophotometer cuvettes together with the polymer blocks. The cuvettes were positioned so that their clear faces were perpendicular to the direction of the lamps and the frosted faces were blacked out. After irradiation the solutions were diluted with 0.25 M KOH in alcohol and the product was estimated as its anion from the absorbance at 458 nm ($\epsilon = 7600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [6, 7].

The electron spin resonance (ESR) experiments were performed using a Varian E104 or alternatively a Bruker B-R70 instrument. Samples were cut from the polymer sheets and sanded to give approximately cylindrical pieces which fitted quartz nuclear magnetic resonance tubes held inside the cavity. Illumination was provided *in situ* using a 200 W Hg-Xe arc lamp except for the experiment where the rates of decay of the ESR signal and the 320 nm absorption peak were compared. In this case samples cut appropriately for each spectrometer were irradiated in the Rayonet reactor prior to spectroscopic examination.

3. Results and discussion

3.1. Azoxybenzene as solute

Absorption spectroscopy showed that this solute (and indeed all the others mentioned in this paper) were incorporated unchanged into the polymeric solution when the monomer was polymerized. Qualitatively, irradiation of PMMA solutions of azoxybenzene caused the initially colourless material to turn yellow, indicating the formation of *o*-hydroxyazobenzene [5]. This was confirmed by absorption spectroscopy, as shown in Fig. 1, from which it can be seen that product formation can be monitored at wavelengths of 420 nm and above without interference due to the absorption of the starting material. Thus it became possible to design an actinometer based on this chemical reaction with photoreactivity in the 300 - 400 nm region, where azoxybenzene absorbs strongly, and product formation monitored in the visible region.

The formation of the product was now followed as a function of time. Figure 2 shows the results for irradiation of a polymer block 3 mm thick containing azoxybenzene at a concentration of 5.0 mg ml^{-1} . It is immediately apparent that the formation of the product does not show a linear dependence on time and that the product yield at long irradiation times falls far short of complete conversion of reactant. This is easy to explain in qualitative terms. Both reactant and product absorb strongly at the exciting wavelength. Since concentrations were deliberately arranged for complete light absorption, light does not penetrate very far into the polymer. Indeed, when irradiated polymer blocks were viewed edge-on it was seen that all the yellow colour of the product was observed near the front face of the block, the rest of the block being colourless.

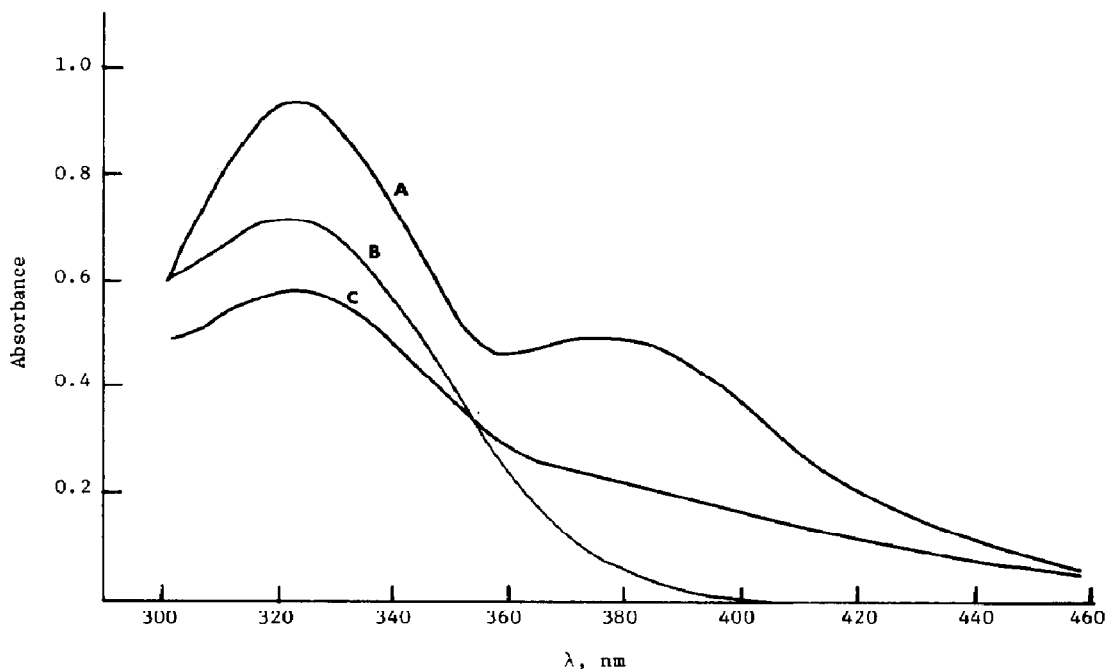


Fig. 1. Spectra of 5.0×10^{-5} M *o*-hydroxyazobenzene in methyl methacrylate (curve A), 1.65×10^{-4} M azoxybenzene in a PMMA block 3 mm thick (curve B) and polymer B irradiated to partial conversion (curve C).

A model for the progress of the reaction as a function of photon flux absorbed was now developed (see Appendix A for the derivation and assumptions). The following equations are two important relationships from this model:

$$f = \exp\{-2.3\epsilon\phi I_0 t \exp(-2.3\epsilon R l)\} \quad (1)$$

$$P = \frac{1}{d} \left\{ \phi I_0 t - \frac{2.3\epsilon(\phi I_0 t)^2}{4} + \frac{(2.3\epsilon)^2(\phi I_0 t)^3}{41.4} - \dots \right\} \quad (2)$$

where f is the fraction of unreacted reactant in an element of the polymer of thickness dl at time t , ϵ is the molar absorptivity of the reactant at the exciting wavelength, ϕ is the quantum yield of the reaction, I_0 is the photon flux per unit area of the polymer face per unit time, R is the initial concentration in moles per decimetre cubed of the reactant, l is the depth of the element dl from the front face of the block, P is the product concentration in moles per decimetre cubed averaged over the whole block and d is the depth of the polymer block.

From these equations we can deduce the following.

(i) Equation (1) shows why product formation falls off very rapidly with depth since it is a double exponential.

(ii) The desired quantity I_0 is not easily extracted from eqn. (2). This is because we know already (Fig. 2) that eqn. (2) cannot be truncated at the

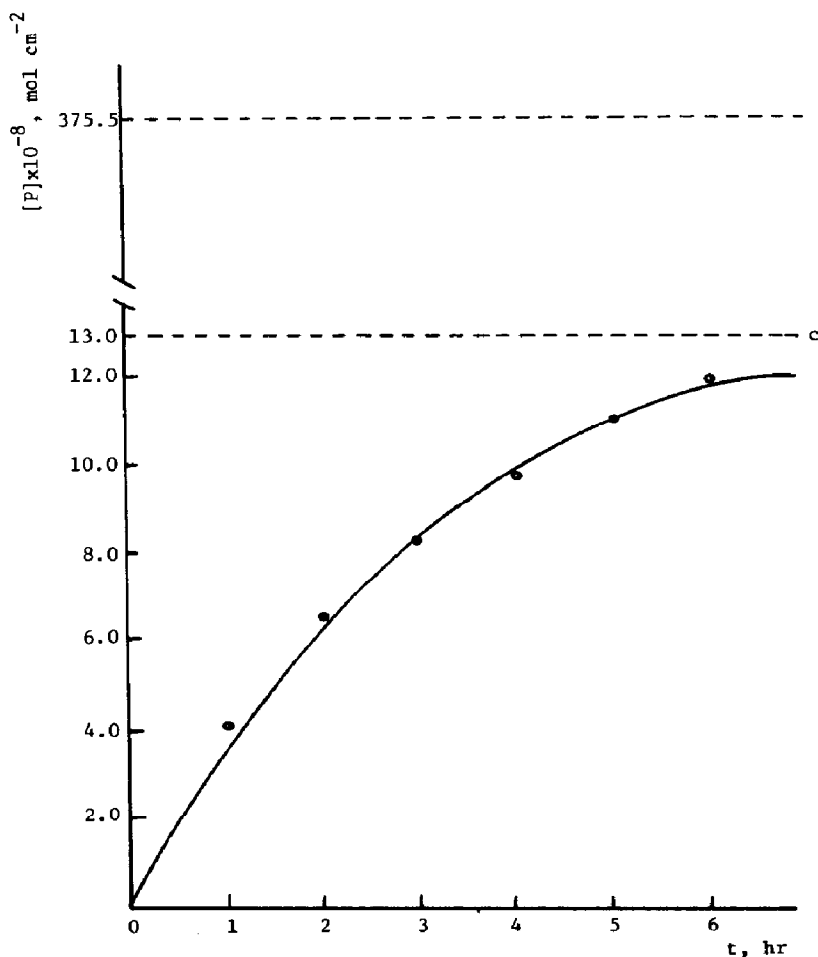


Fig. 2. Time dependence of the production of *o*-hydroxyazobenzene upon irradiation of a PMMA block 3 mm thick containing 5.0 mg azoxybenzene ml⁻¹.

first term, and the higher order terms in t are of equally high order in I_0 . (Actually, insertion of experimental data into eqn. (2) shows that this function is not rapidly convergent.)

(iii) In eqn. (2) P is expressed conventionally in units of moles per decimetre cubed. If, however, product formation is expressed in moles per unit area as p equivalent to $P \times d$, we see that p is independent of both the initial concentration of reactant in the polymer and of the depth of the polymer block.

Although conclusion (ii) seems to rule out this method for determining photon flux, we discovered empirically that the data of Fig. 2 can be fitted to the much simpler function

$$\ln\left(1 - \frac{p}{c}\right) = -\frac{\phi I_0 t}{c} \quad (3)$$

This equation is identical with the form obtained in homogeneous fluid solution when an initial concentration c is converted with time into product and equal molar absorptivities are assumed for the reactant and the product (*cf.* ref. 8). Both p and c are expressed in moles per unit area of surface (equivalent to concentration \times polymer thickness) as discussed in (iii). However, to obtain a good empirical fit, c is not the initial concentration of azoxybenzene per unit area. Instead, c is an adjustable parameter whose optimum value is determined by trial and error. Excellent fits to eqn. (3) were obtained in this manner (Fig. 3).

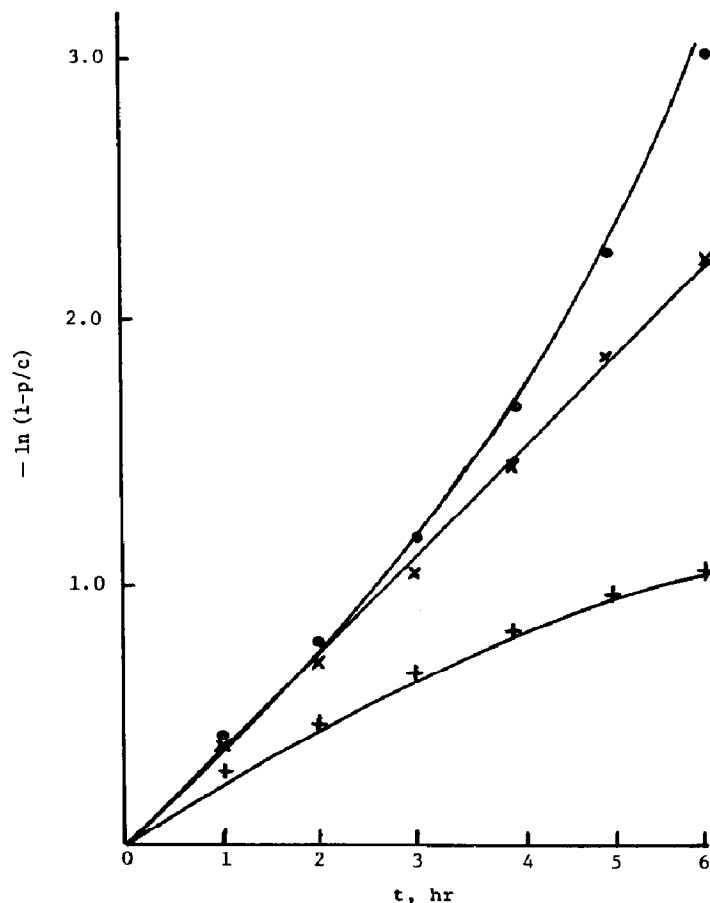


Fig. 3. Plots of $-\ln(1 - p/c)$ vs. time for the irradiation of a PMMA block 3 mm thick containing 5.0 mg azoxybenzene ml^{-1} showing the fit to various trial values of c : \circ , $c = 1.22 \times 10^{-7}$; \times , $c = 1.3 \times 10^{-7}$, $r = 0.994$; $+$, $c = 1.8 \times 10^{-7}$.

The success of this approach was confirmed when irradiations were made using polymers of varying thickness and solute concentration. As seen in the raw data of Table 1, the rate of formation of the product is independent of both polymer thickness and solute concentration. This is to be expected when the complete analysis of eqn. (2) is considered. In terms of the empirical analysis it means that parameter c has the same value for all the

TABLE 1

Production of *o*-hydroxyazobenzene in the photolysis of various azoxybenzene-poly-(methyl methacrylate) solutions as a function of time

[Azoxybenzene] (mg ml ⁻¹)	0.5	1.0	2.0	3.0	4.0	5.0
Polymer thickness (mm)	5	4	4	5	4	3
<i>Run 1</i>	[<i>o</i> -hydroxyazobenzene] (×10 ⁻⁷ mol cm ⁻²)					
<i>t</i> = 0	0	0	0	0	0	0
<i>t</i> = 2 h	0.76	0.68	0.71	0.74	0.73	0.71
<i>t</i> = 3 h	0.94	0.85	0.86	0.89	0.92	0.88
<i>t</i> = 4 h	1.07	0.99	1.04	1.05	1.09	1.02
<i>t</i> = 5 h	1.17	1.07	1.12	1.13	1.22	1.11
<i>t</i> = 6 h	1.23	1.13	1.19	1.20	1.30	1.22
<i>t</i> = 7 h	1.27	1.15	1.22	1.23	1.34	1.24
<i>c</i> (×10 ⁻⁷ mol cm ⁻²)	1.3	1.2	1.3	1.3	1.4	1.3
Slope (×10 ⁴ cm ² mol ⁻¹)	3.9	3.5	3.0	3.1	3.4	3.3
<i>r</i>	0.996	0.999	0.999	0.999	0.998	0.996
<i>I</i> ₀ (×10 ⁻⁵ mol cm ⁻² h ⁻¹)	1.4	1.4	1.4	1.4	1.4	1.4
$\phi \times 10^3$	5.1	4.1	3.9	4.1	4.7	4.3
<i>Run 2</i>	[<i>o</i> -hydroxyazobenzene] (×10 ⁻⁷ mol cm ⁻²)					
<i>t</i> = 1 h	0.45	0.46	0.46	0.39	0.45	0.41
<i>t</i> = 2 h	0.67	0.69	0.69	0.64	0.73	0.66
<i>t</i> = 3 h	0.85	0.85	0.80	0.79	0.87	0.84
<i>t</i> = 4 h	1.04	0.97	0.93	0.92	0.97	0.99
<i>t</i> = 5 h	1.13	1.04	1.01	1.01	1.09	1.09
<i>t</i> = 6 h	1.21	1.11	1.07	1.11	1.16	1.16
<i>c</i> (×10 ⁻⁷ mol cm ⁻²)	1.3	1.2	1.2	1.2	1.3	1.3
Slope (×10 ⁴ cm ² mol ⁻¹)	3.5	3.4	2.9	3.3	2.9	3.0
<i>r</i>	0.994	0.998	0.998	0.993	0.998	0.999
<i>I</i> ₀ (×10 ⁻⁵ mol cm ⁻² h ⁻¹)	1.3	1.3	1.3	1.3	1.3	1.3
$\phi \times 10^3$	4.5	4.0	3.5	3.9	3.8	3.9

polymer samples investigated. Since this is true, then the photon flux is readily obtained from the slope of the line obtained by plotting $\ln(1 - p/c)$ versus time. Once this has been determined it follows that the integrated photon flux $I_0 t$ can be obtained from a single absorption measurement, provided that irradiation is not carried on so long that p approaches too closely the apparent asymptote c marked on Fig. 2.

The physical picture behind these results is interesting. Because of the constancy of parameter c it follows that the polymer solution behaves as if there were a slice of the polymer block beginning at the front face with the properties of a fluid solution conforming to eqn. (3). This slice is of a sufficient depth to contain c moles of azoxybenzene per unit area and varies in depth according to the actual concentration of azoxybenzene that is present. Any depth of polymer beyond this slice behaves as an inert transparent backing. By applying Beer's law to the experimental value of $c = 1.3 \times 10^{-7}$ mol cm⁻² we deduce that this pseudofluid region of the polymer is of such a depth as to have an absorbance of about 1.9.

Several experimental determinations of ϕ for the photorearrangement of azoxybenzene were made for various polymer samples. These were made by using the photorearrangement of azoxybenzene in ethanol ($\phi = 2.5 \times 10^{-2}$ at 348 nm [5]) as the actinometer and applying eqn. (3) to the polymer (the empirical value of c was used). These results are given in Table 2. Overall, ϕ_{polymer} was calculated from a total of 19 such determinations to be $(4.2 \pm 0.2) \times 10^{-3}$ (Table 3). Since ϕ is constant for a known I_0t it follows that, if ϕ is used as the known parameter, I_0t is obtained by the reverse procedure. We thus believe that these results establish the solid solution of azoxybenzene as a practical actinometer system for the near-UV region.

TABLE 2

Quantum yield determinations for azoxybenzene-poly(methyl methacrylate) versus azoxybenzene in alcohol

Irradiation time (h)	0.50	0.75	0.50	0.75	0.75	0.50	0.33
$A_{458 \text{ nm}}$ (solution)	0.336	0.478	0.292	0.406	0.434	0.296	0.181
[<i>o</i> -hydroxyazobenzene] ($\times 10^{-4}$ M)	3.84	5.46	3.33	4.63	4.95	3.38	2.07
[<i>o</i> -hydroxyazobenzene] ($\times 10^{-7}$ mol cm $^{-2}$)	1.86	2.64	1.61	2.24	2.40	1.63	1.00
I_0t ($\times 10^{-6}$ mol cm $^{-2}$)	7.4	10.5	6.4	9.0	9.6	6.5	4.0
$c_{\text{azoxybenzene-PMMA}}$ (mg ml $^{-1}$)	0.5	0.5	1.0	1.0	2.0	4.0	4.0
$A_{420 \text{ nm}}$ (polymer)	0.250	0.326	0.224	0.345	0.334	0.245	0.134
[<i>o</i> -hydroxyazobenzene] ($\times 10^{-8}$ mol cm $^{-2}$)	2.78	3.62	2.49	3.83	3.71	2.72	1.49
c ($\times 10^{-7}$ mol cm $^{-2}$)	1.3	1.3	1.3	1.3	1.3	1.3	1.3
$-\ln(1 - p/c)$	0.24	0.33	0.21	0.35	0.34	0.23	0.12
$\phi \times 10^3$	4.2	4.0	4.3	5.0	4.5	4.7	4.0

TABLE 3

Average quantum yield values

Experiment ^a	$\phi \times 10^3$
Table 1, run 1 (6)	4.36 ± 0.29
Table 1, run 2 (6)	3.93 ± 0.16
Table 2 (7)	4.39 ± 0.25

^a The number of measurements performed is given in parentheses.

The following protocol allows the total photon flux I_0t to be determined from the absorbance measurement. Its units are einsteins per centimetre squared.

(i) We measure the absorbance A of the product at 420 nm. If both faces of the polymer block were irradiated simultaneously, we divide by 2.

The corrected absorbance A^1 should not exceed 0.5, or the ratio p/c in eqn. (3) will be too close to unity.

(ii) We substitute into eqn. (3)

$$I_0 t = -c\phi^{-1} \ln\left(1 - \frac{p}{c}\right)$$

When we evaluate the constants c and ϕ and substitute $p = A^1/1000\epsilon$, where p is in moles per centimetre squared, we obtain

$$I_0 t = -3.1 \times 10^{-5} \ln(1 - 1.71A^1) \quad (4)$$

In summary, polymerization of solutions of azoxybenzene in methyl methacrylate produces a solid sheet which is useful as a chemical actinometer. Clear blocks can be cut from these sheets, illumination of which in the near-UV region causes the production of *o*-hydroxyazobenzene. The yellow colour of this product allows the reaction to be monitored at a wavelength removed from the region of azoxybenzene absorption. A single absorbance measurement then permits the calculation of the incident photon flux, provided that product formation has not approached the limiting value too closely. Since azoxybenzene is strongly absorbent in the UV but not in the visible region, the polymer solutions can be handled briefly in diffuse room light. With a quantum yield of 4×10^{-3} the new actinometer may find applications in situations where the *o*-nitrobenzaldehyde actinometer is too photoreactive.

3.2. Other solutes

We investigated other solutes for use as actinometers in PMMA solution. These included benzophenone, 1,3-diphenylpropanone and *o*-nitrobenzaldehyde. The last of these was the system used by Cowell and Pitts [1] in the thin film technique. In the former two cases we hoped to follow the progress of the photoreaction by monitoring the disappearance of the $^1n,\pi^*$ absorption band of the ketone. In neither of these cases could a successful actinometer be developed because of unexpected absorbance changes in the 300 - 350 nm region. These were most pronounced for benzophenone where the absorbance at $\lambda_{\max}(n,\pi^*) = 335$ nm increased sharply on brief irradiation. This increased absorbance decayed away slowly in the dark over a period of several weeks, following a rate law that was second order in the decay of "transient" absorbance ($r = 0.996$ at 1460 h).

When the irradiated polymer containing benzophenone solute was examined using ESR spectroscopy, a strong spectrum was obtained. This was identical with the spectrum obtained on irradiating PMMA at 254 nm [9]. This spectrum is attributed [9] to radicals formed by the addition of some radical species X to the residual monomer in the polymer. This problem arises because in our technique relatively massive polymer blocks are

TABLE 4

Signal strength of the radical $-\text{CH}_2-\dot{\text{C}}(\text{CH}_3)-\text{CO}_2\text{CH}_3$ formed on photolysis of various solutes in poly(methyl methacrylate)

<i>Solute</i>	<i>Relative signal strength</i>
Ph_2CO	1.0 ^a
$\text{PhCH}_2\text{COCH}_2\text{Ph}$	0.6
<i>o</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	0.6
Azoxybenzene	< 0.05
No solute ^b	0.3

^a Assumed.

^b Contains benzoyl peroxide initiator and decomposition products.

prepared by polymerizing methyl methacrylate in which the solute is already dissolved, and such polymers always contain residual monomer [9]. The purification step performed by Cowell and Pitts [1] eliminates this problem. We demonstrated that the increased absorbance at about 335 nm is due to this radical because during a period of 10 h the percentage decay of the UV absorbance and the ESR signal were identical within the limits of the experiment.

Table 4 gives the relative strength of the ESR signal of this radical for various solutes all irradiated under the same conditions for similar times. Benzophenone, diphenylacetone and *o*-nitrobenzaldehyde all give easily detectable ESR signals. All these solutes undergo photochemical reaction through triplet excited states and consequently have the opportunity to exhibit radical-like character. This is particularly well known for benzophenone [10]. For diphenylacetone the reaction involves cleavage [11] and presumably both caged and free radicals intervene. For *o*-nitrobenzaldehyde we can likewise suppose that intermolecular hydrogen abstraction from the solvent competes, at least to some extent, with hydrogen abstraction from the formyl group by the nitro function [12]. Notable in this list is the azoxybenzene-PMMA system from which no radical signals could be detected. The azoxybenzene photorearrangement differs from the others in that it is known to proceed from the singlet state [6] and does not involve radical intermediates [7].

We can now indicate which reactions might be suitable for study in relatively massive blocks of PMMA. All reactions involving radical intermediates will be unsuitable because the radicals formed will be trapped by unreacted monomer and produce long-lived adducts whose absorption at 320 - 350 nm will interfere with the absorption of light by reactants which absorb in the near-UV region. It is the absence of radical intermediates which makes azoxybenzene a suitable photoreactive chemical for this kind of actinometer.

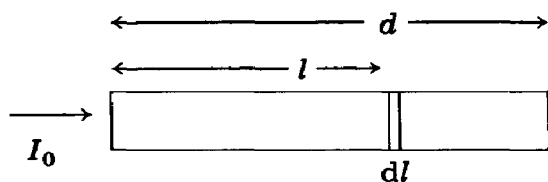
Acknowledgments

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Appendix A



The following symbols are used in addition to those defined in Section 3: l and dl are as shown above; I is the light intensity per unit area received at depth l ; $dI_{\text{abs, T}}$ and $dI_{\text{abs, R}}$ are the light intensities per unit area absorbed by all components and by the unchanged reactant respectively in an element of thickness dl ; δP (δR) is the concentration in moles per decimetre cubed of the product (reactant) in an element of thickness dl at time t ; R is the initial concentration of the reactant in moles per decimetre cubed.

The following assumptions are made.

(1) At all times only reactant and product are present, *i.e.* the product is formed quantitatively.

(2) $\epsilon_{\text{reactant}} = \epsilon_{\text{product}} = \epsilon$ at the exciting wavelength. This assumption means that the light intensity at any depth is constant with time. (In the general case where $\epsilon_{\text{product}} \neq \epsilon_{\text{reactant}}$ the expression for $dI_{\text{abs, R}}$ is substantially more complex:

$$dI_{\text{abs, R}} = I_0 \exp[-2.3\{\epsilon_{\text{reactant}}R + (\epsilon_{\text{product}} - \epsilon_{\text{reactant}})(P_{\text{average}})_0^i\}l] \times \\ \times 2.3\epsilon_{\text{reactant}}(R - \delta P) dl$$

We were then unable to integrate the resulting expression for ϕ with respect to δP .)

We consider the element dl : the light received at depth l per unit area is

$$I = I_0 10^{-\epsilon R l} = I_0 \exp(-2.3\epsilon R l)$$

the light absorbed in dl per unit area is

$$dI_{\text{abs, T}} = I - I \exp(-2.3\epsilon R dl) = 2.3\epsilon I R dl$$

the light absorbed by the reactant in dl per unit area is

$$dI_{\text{abs, R}} = 2.3\epsilon I R \left(\frac{\delta R}{\delta R + \delta P} \right) dl = 2.3\epsilon I (R - \delta P) dl$$

$$\phi = \frac{\text{moles/area product formed per unit time}}{\text{moles/area photons absorbed by reactant per unit time}}$$

$$= \frac{d}{dt} (\delta P) dl / dI_{\text{abs, R}}$$

$$= \frac{d}{dt} (\delta P) / 2.3\epsilon I (R - \delta P)$$

$$\int_0^{\delta P} \frac{d(\delta P)}{R - \delta P} = \int_0^t 2.3\epsilon \phi I dt$$

$$\ln \left(\frac{R - \delta P}{R} \right) = \ln f = -2.3\epsilon \phi I t$$

$$f = \exp\{-2.3\epsilon \phi I_0 t \exp(-2.3\epsilon R l)\} \quad (\text{A1})$$

The average fraction of reactant not converted in the block is

$$F = \frac{1}{d} \int_0^d f dl$$

Expanding the $\exp(\exp x)$ expression as a power series and integrating term by term gives

$$\begin{aligned}
 F &= \frac{1}{d} \left\{ l + \frac{2.3\epsilon\phi I_0 t \exp(-2.3\epsilon Rl)}{2.3\epsilon R} - \frac{(2.3\epsilon\phi I_0 t)^2 \exp(-4.6\epsilon Rl)}{4.6\epsilon R \times 2!} + \right. \\
 &\quad \left. + \frac{(2.3\epsilon\phi I_0 t)^3 \exp(-6.9\epsilon Rl)}{6.9\epsilon R \times 3!} \dots \right\}_0^d \\
 &= 1 - \frac{\phi I_0 t}{Rd} \{1 - \exp(-2.3\epsilon Rd)\} + \frac{2.3\epsilon(\phi I_0 t)^2}{4Rd} \{1 - \exp(-4.6\epsilon Rd)\} - \\
 &\quad - \frac{(2.3\epsilon)^2(\phi I_0 t)^3}{41.4Rd} \{1 - \exp(-6.9\epsilon Rd)\} \dots
 \end{aligned}$$

$F = 1 - Pd/Rd = 1 - P/R$ which is observable and all the $1 - \exp(nA)$ terms approach unity for high absorbances. Therefore

$$p = Pd = \phi I_0 t - \frac{2.3\epsilon(\phi I_0 t)^2}{4} + \frac{(2.3\epsilon)^2(\phi I_0 t)^3}{41.4} \dots \quad (\text{A2})$$

To evaluate this expression and leave p in units of moles per square centimetre of surface, the conventional value of ϵ in units of decimetres cubed per centimetre per mole must be converted to centimetres squared per mole by multiplying by 1000 wherever ϵ appears in eqn. (2). Likewise, to obtain p directly from absorbance measurements on the polymer block the expression $p = A/1000\epsilon$ is used where p is in moles per centimetre squared.