the results obtained here for Ru(bpy)$_3^{2+}$ to our earlier results obtained for Os(bpy)L$_4^{2+}$, values of E_{em} have been used since the dependence of E_{em}(0–0) on E_{em} is very similar for both systems. As a result of the substitution of E_{em} for E_{em}(0–0), the absolute values of the intercepts of plots of ln k_{nr} vs. E_{em} will be shifted by an amount $-b\gamma_0/\hbar\omega_M$ from those observed when ln k_{nr} is plotted against E_{em}(0–0). Since the magnitude of b is comparable for Ru(bpy)$_3^{2+}$ and Os(bpy)L$_4^{2+}$, the magnitude of the difference in the intercepts, which can be related to the difference in the vibrationally induced electronic coupling term C^2 for the Ru and Os excited states, will be unaffected by the substitution of E_{em} for E_{em}(0–0).

Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; dichloromethane, 75-09-2; *n*-butyronitrile, 109-74-0; pyridine, 110-86-1; acetonitrile, 75-05-8; propylene carbonate, 108-32-7; *N,N*-dimethylformamide, 68-12-2.

Supplementary Material Available: Tables of the temperature dependence of the excited-state lifetime of [Ru(bpy)$_3$](PF$_6$)$_2$ in the six solvents used in this study (6 pages). Ordering information is given on any current masthead page.

Distribution of Site Reactivities in Photoreactive Amorphous Solids

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Abstract: The kinetics of photoprocesses in amorphous solids are determined by the distribution of reactivities over an ensemble of matrix sites. A method is described which allows the estimation of reactivity distributions from the dependence of the macroscopic quantum yield of the photoreaction on the degree of reactant conversion. The procedure is illustrated on three industrial photopolymers and is shown to provide in this instance a useful insight into the molecular mechanism of cross-link formation.

In recent years the photochemistry of amorphous solids has attracted attention partly because of the industrial uses of solid-state photochemistry[1-3] and partly because of the information provided by photochemical probes into the structure and the molecular dynamics of solid polymers.[4-14]

In the solid phase, the environment of a reactant influences the chemical process by its physical presence or by direct participation in the chemistry. The reactant cannot, therefore, be considered in isolation, but it must be taken together with its immediate surroundings.[15,16] This approach leads to the concept of reactant sites and to a view of the photoreactive matrix as an ensemble of such sites.

On a molecular scale the ensemble of chromophore sites may be described by a distribution of site properties. If the distribution function of a particular site property is known, the corresponding macroscopic property of the solid may be derived from it. Property distributions exist in all unordered systems, but there is in this respect a fundamental difference between fluids and solids: in fluids, time averaging ensures the approximate constancy of the distribution, so that these systems can be treated as if they consisted of identical molecules of unchanging average properties. In solids, by contrast, the distribution of site properties may change drastically in the course of the chemical process, and with it property averages and the macroscopic behavior of the system. The distribution of site properties in a solid matrix is therefore of practical interest.

This paper is concerned with site reactivities. Their distribution determines the overall photokinetic behavior of the solid and as a consequence it should be possible to determine reactivity distributions from experimentally observed reaction rates. Kryszewski et al.[17] were the first to show how an inference of this kind can be made. They studied the thermal isomerization of a photochromic probe in a group of polymer films, and from the bleaching kinetics of the probe they were able to derive free volume distributions in the host matrices.

We have now found that the distribution of site reactivities may be inferred from the change of quantum yield during irradiation of a photoreactive solid. It is generally observed[18-20] that in amorphous solids the quantum yield of a photoreaction decreases as irradiation progresses. Figure 1 shows a typical example. It refers to a film of poly(vinyl cinnamate), a photopolymer in which cycloaddition between adjacent cinnamoyl groups[21] occurs on irradiation. In the figure, the quantum yield of the reaction, ϕ, is plotted as a function of the degree of conversion, x, of the chromophores and can be seen to decrease rapidly with increasing conversion.[22,23] This behavior is attributed to the preferential

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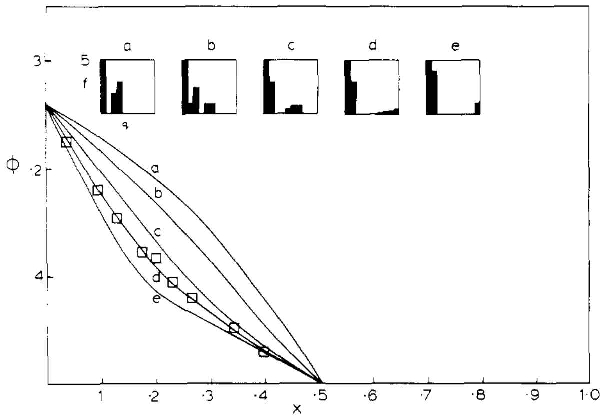

Figure 1. Curves of ϕ vs. x for the assumed reactivity distributions represented in the histograms. All satisfy the initial conditions $\sum f_i = 1$, $\phi(0) = 0.26$, $\bar{n} = 1$, $f_0 = 0.5$. The experimental points refer to an unsensitized film of poly(vinyl cinnamate) exposed to 300-nm radiation.

depletion of the more reactive sites in the early stages of the process. The macroscopic quantum yield which reflects the average reactivity of the surviving chromophore sites decreases as the more reactive sites are being removed from the ensemble.

In the following sections the quantitative link between the reactivity distribution and the quantum yield function $\phi(x)$ will be established, and reactivity distributions will be estimated for three representative industrial photopolymers.

The Statistics of the Matrix Reaction

Consider an ensemble of sites divided into groups in such a way that the sites within each group have nearly identical properties. For example, all sites of group i have, in the excited state, the reaction probability ρ_i and the decay probability λ_i. The sites in group i are a fraction f_i of the total number of sites. The set of f_i values corresponding to the full range of ρ is the distribution function of the site reactivities.

If a photon is introduced into the ensemble, it will promote one of the chromophores into an excited state. After that, one of three alternative events may occur: (i) the chromophore may react (probability ρ_i); (ii) it may return to the ground state (probability λ_i); or (iii) it may hand over the excitation to a neighboring chromophore (probability $1 - \rho_i - \lambda_i$).

Let us assume that in N transfer steps the quantum of excitation makes n_i visits to sites of group i and that it reacts on the $(N + 1)$th visit at a site of group j. The probability of this event is

$$P_N = f_j\rho_j \sum^{N} [\Pi(1 - \rho_i - \lambda_i)^{n_i} f_i^{n_i}] \frac{N!}{\Pi n_i} \qquad (1)$$

where the summation extends over all possible sets of n_i. The series is the multinomial expansion and can be written in the form

$$P_N = f_j\rho_j[\textstyle\sum(1 - \rho_i - \lambda_i)f_i]^N \qquad (2)$$

The probability that a quantum will react at a j site in any visit is the sum of (2)

$$P_j = \sum P_N = \frac{f_j\rho_j}{\sum f_i(\rho_i + \lambda_i)} \qquad (3)$$

Since, by definition $\sum f_i = 1$, the probability that the quantum will react at all (at any step, at any site) is found by summing over all sites.

$$P = \sum P_j = \frac{\sum f_j\rho_j}{\sum f_i\rho_i + \sum f_i\lambda_i} \qquad (4)$$

The average number of migratory steps ($\bar{n}$) which the quantum executes as it passes from site to site is obtained as the expectation value of the number of visits, in the form

$$\bar{n} = \sum f_i(\rho_i + \lambda_i)\sum_{0}^{\infty}(N + 1)[\textstyle\sum(1 - \rho_i - \lambda_i) f_i]^N \qquad (5)$$

After straightforward algebra, the result of summing this series is

$$\bar{n} = [\textstyle\sum f_i(\rho_i + \lambda_i)]^{-1} \qquad (6)$$

If no migration occurs in the system, the sum $(\rho_i + \lambda_i)$ is always unity, and hence $\bar{n}$ is equal to unity, as would be expected. If a certain class of sites acts as traps, then for these sites $(\rho_t + \lambda_t)$ is also unity.

Taking energy migration into account, we may write for the probability of reaction at a site of group j (eq 3)

$$P_j = \bar{n} f_j \rho_j \qquad (7)$$

so that the effective reactivity of a j site is $\bar{n}\rho_j$. It is important to note (see eq 6) that $\bar{n}$ depends here on the values of f_i which change during irradiation as the composition of the ensemble changes.

With these preliminaries completed we can now turn to the problem of describing the overall rate at which reaction occurs. If at time t after the onset of irradiation the fraction x of the chromophores has reacted, out of a total of N_0 sites, then

$$1 - x(t) = \frac{1}{N_0}\sum n_i = \sum f_i \qquad (8)$$

The number of sites $\mathrm{d}n_s$ of type s which react during the time interval $\mathrm{d}t$ is given by the product of the probability that an s site absorbs a photon from a total absorbed flux Q and the reactivity ρ_s of an s site.

$$\mathrm{d}n_s = -2Q\frac{n_s}{N_0(1 - x)}\bar{n}\rho_s\,\mathrm{d}t \qquad (9)$$

(We have introduced the factor 2 in eq 9 because in the examples which we shall present later, the reaction removes simultaneously two chromophores from the ensemble.)

If we define an auxiliary quantity $w(t)$ by

$$w(t) = 2\int_0^t \frac{\bar{n}(t)Q}{N_0(1 - x)}\,\mathrm{d}t \qquad (10)$$

integration of eq 9 leads to the result

$$n_s(t) = n_s(0)\exp(-w\rho_s) \qquad (11)$$

or, for a fractional distribution of chromophore sites

$$f_s(t) = f_s(0)\exp(-w\rho_s) \qquad (12)$$

The quantum yield of the photoreaction is defined by the expression

$$\phi(t) = 2\frac{\sum n_s\bar{n}\rho_s}{N_0(1 - x)} = 2(1 - x)^{-1}\sum\bar{n}\rho_s f_s(0)\exp(-w\rho_s) \qquad (13)$$

Initially one has

$$\phi(0) = 2\sum\bar{n}(0)\rho_s f_s(0) \qquad (14)$$

An expression for $x(t)$ is obtained from (8) and (12)

$$1 - x(t) = \sum f_s(0)\exp(-w\rho_s) \qquad (15)$$

which for $x = 0$ leads correctly to $\sum f_s(0) = 1$.

Equations 13 and 15 relate the quantum yield with the degree of conversion in terms of the distribution of site reactivities. They enable us to calculate the quantum yield function $\phi(x)$ for any given distribution of site reactivities. By generating for a particular system the quantum yield functions of a set of assumed distributions and comparing the result with the experimental $\phi(x)$ curve, it is possible to determine an approximate reactivity distribution for the real system.

It will be noted that in eq 13 and 15 the average number of migratory steps $\bar{n}$ is a function of f_s. These fractions themselves

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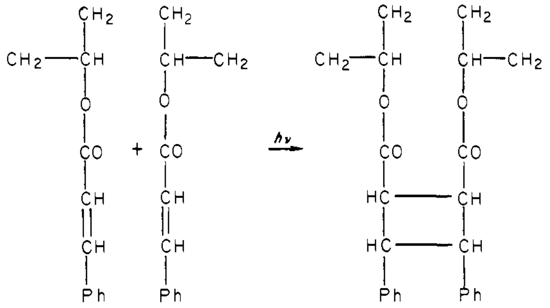
Scheme I



change during the course of the photoreaction in accordance with eq 12. The evaluation of eq 13 and 14 in all generality is therefore not straightforward. It is, however, always possible to devise an iterative procedure to deal with such a situation, but this is a laborious undertaking and can be justified only in exceptional cases. Here we shall illustrate a simplified procedure which is appropriate when one or the other of the variables of the system is limited to a narrow variation range. This simplified method will be demonstrated on three representative photopolymers.

A Photopolymer in Which Energy Migration Does Not Occur

Poly(vinyl cinnamate) is cross-linked on irradiation by a photocycloaddition reaction schematically indicated in Scheme I. Because of the very short lifetime of the singlet excited state of the cinnamoyl groups, singlet excitation energy does not migrate in the poly(vinyl cinnamate) matrix.[23] We note from the experimental data[23] that in direct excitation (i.e. in the absence of a triplet sensitizer), the initial yield of the photoreaction is $\phi(0) = 0.26$.

The evaluation of the quantum yield function is based on eq 13 where we put $\bar{n} = 1$. The chromophore sites are divided into groups with the reactivities ρ_i equal to 0, 0.1, 0.2, ..., 0.9. Introducing the auxiliary variable

$$\theta = \exp(-0.1w) \tag{16}$$

eq 15 may be written in the form

$$1 - x = \sum_{0}^{9} f_s(0)\theta^s \tag{17}$$

and eq 13 becomes

$$\phi = 2(1 - x)^{-1}\sum_{0}^{9} \rho_s f_s(0)\theta^s \tag{18}$$

The values of f_s must of course satisfy the initial conditions (14) and $\sum f_s = 1$, in particular

$$2\sum_{0}^{9} \rho_s f_s(0) = 0.26$$

In these expressions θ acts merely as a parameter. Thus, if we specify a trial distribution f_s, eq 17 and 18 can be immediately evaluated for different choices of θ and in this way the ϕ vs. x relation can be constructed.

The outcome of this procedure is shown in Figure 1 for several trial distributions, each of which satisfies the initial conditions. It can be seen that distribution *d* fits the observations most closely and is therefore the nearest approximation to the reactivity distribution in the real polymer matrix.

A Photopolymer with Moderate Energy Migration

In a polymer where energy migration is confined to a small number of transfer steps, and where the migration range does not change appreciably during the course of the reaction, it is possible, as a first approximation, to replace $\bar{n}(t)$ by its initial value $\bar{n}(0)$ which applies at the onset of irradiation.

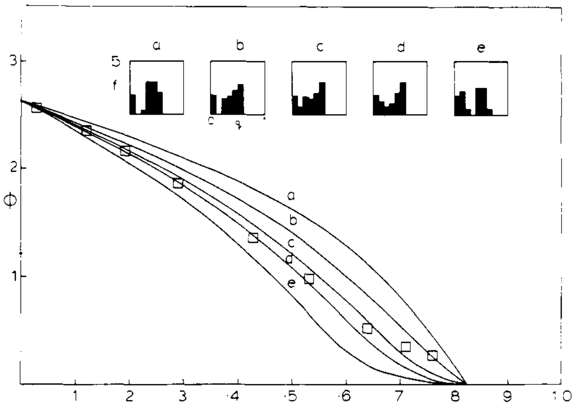


Figure 2. Curves of ϕ vs. x for the assumed reactivity distributions shown in the histograms. They satisfy the initial conditions $\sum f_i = 1$, $\phi(0) = 0.26$, $\bar{n} = \bar{n}(0) = 2$, $f_0 = 0.15$. The experimental points refer to a photoreactive polyester of *p*-phenylenediacrylic acid exposed to 330-nm radiation.

If the assumption $\bar{n}(t) = \bar{n}(0)$ is made, two new variables can be defined

$$r_s = \bar{n}(0)\rho_s \tag{19}$$

and

$$\chi = \exp(-w/\bar{n}(0)) \tag{20}$$

The quantum yield and the degree of chromophore conversion can then be expressed in the new terms

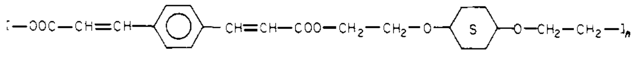
$$\phi = 2(1 - x)^{-1}\sum r_s f_s(0)\chi^{r_s} \tag{21}$$

and

$$(1 - x) = \sum f_s(0)\chi^{r_s} \tag{22}$$

Equations 21 and 22 replace eq 17 and 18 and together with the initial conditions provide the desired relation between ϕ and x. It will be noted that here the value of r_s is not necessarily less than unity since the fractional reactivity is multiplied by the initial number $\bar{n}(0)$ of migratory steps.

The preconditions for this treatment are fulfilled in a photoreactive polyester of *p*-phenylenediacrylic acid[24]



On direct irradiation of a film of this photopolymer a chromophore conversion of up to 85% can be achieved, and the initial quantum yield of cycloaddition[25] is $\phi(0) = 0.26$. We know from fluorescence spectroscopy[26] and from chemical analysis[25] that about half of all chromophores in the film are located at excimer sites and that these sites represent energy traps. Furthermore, the fluorescence spectrum of the solid polymer films indicates that in the early stages of irradiation all quanta are trapped at excimer sites. If the fraction of trap sites is 0.5, the initial average number of energy transfer steps must be $\bar{n}(0) = 2$.

In analyzing the $\phi(x)$ curve of this system we have assumed that the initial migration range remains unchanged, and have accordingly used the initial conditions $\phi(0) = 0.26$ $\sum f_s = 1$ and $\bar{n}(0) = 2 = \bar{n}$. The $\phi(x)$ curves for a few distributions compatible with these conditions are shown in Figure 2. Curve d appears to give the best fit with the experimental points; the histogram d is therefore the nearest approximation to the distribution of site reactivities in the polymer. It can be seen, however, that agreement between the model and the experimental results is less good than in the previous examples. Nevertheless, the analysis reveals the main characteristic of the system, namely the absence of any highly reactive sites.

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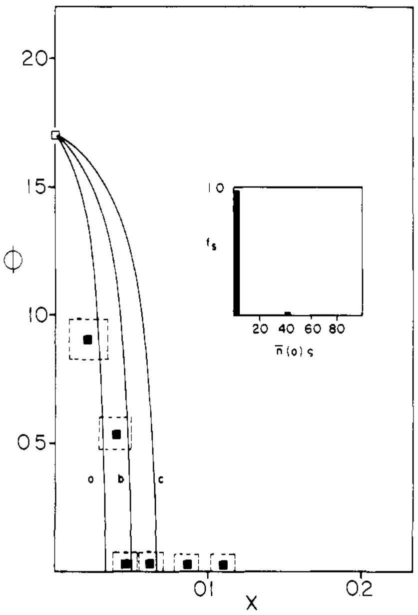


Figure 3. Curves of ϕ vs. x corresponding to the initial conditions $\phi(0) = 1.7, f_r(0) = 0.02, 0.03, 0.04$. Only the histogram for the case $f_r(0) = 0.02$ is shown. The experimental points refer to a triplet-sensitized film of a photopolymer based on the chromophore 1,2-diphenylcyclopropane, exposed to 380-nm radiation.

A Photopolymer with Extensive Energy Migration

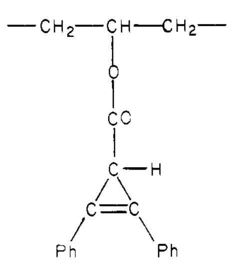
In the presence of extensive energy migration the use of eq 13 and 15 is complicated by the interdependence between $\bar{n}(t)$ and $f_s(t)$. As indicated, a solution cannot be given in closed form for the general case. However, when a single type of reaction site dominates the system, the composition of the subensemble of reactive sites will not change during the reaction, and eq 13 and 15 will take the simple form

$$\phi(t) = 2(1 - x)^{-1} f_r(t) \rho_r \bar{n}(t) \tag{23}$$

$$x = f_r(0) - f_r(t) \tag{24}$$

For a given value of the fraction of reactive sites, f_r, the initial value of the product $\bar{n}(0)\rho_r$ can be derived from $\phi(0)$, and eventually the whole quantum yield function $\phi(x)$ can be calculated.

An example where this procedure may be applied is provided by a photopolymer based on the photoreactive chromophore diphenylcyclopropene.[27] The material is prepared by the partial esterification of poly(vinyl alcohol) with the acid chloride of 1,2-diphenylcyclopropene-3-acetic acid.[28] On sensitization with a triplet sensitizer[29] the initial quantum yield of chromophore consumption by the bimolecular cycloaddition process is found to be $\phi(0) = 1.7$. The quantum yield decreases rapidly during the early stages of irradiation (see Figure 3) and approaches zero when only 2 to 3% of the chromophores have been converted. Evidently, a very small fraction of chromophores occupies reactive sites. A low concentration of reactive sites and a high initial quantum yield can coexist only in the presence of extensive energy migration.



In evaluating $\phi(x)$ for this polymer we have assumed that the few reactive sites in the system have unit reactivity, $\rho_r = 1$. In that case the migration range $\bar{n}(t)$ can be linked to the surviving fraction of reactive sites, $f_r(t)$, by the expression

$$\bar{n}(t) = (f_r(t) + f_d)^{-1} \tag{25}$$

Here f_d is the fraction of sites at which the excitation quantum decays without bringing about a photoreaction.

We have calculated $\phi(x)$ curves for this model and for three initial concentrations of reactive sites (0.02, 0.03, and 0.04). These are shown in Figure 3. It can be seen that $f_r(0) = 0.02$ leads to a quantum yield function which comes closest to the experimental data. The histogram of the site distribution corresponding to $f_r(0) = 0.02$ is shown in the in-set of Figure 3. The essential features of the reactive behavior of the system emerge quite clearly from this simplified treatment.

Summary and Conclusion

From a knowledge of the distribution of site reactivities the quantum yield function of a photoreactive matrix may be derived. A general method for the calculation of the quantum yield and of the corresponding degree of reactant conversion is outlined. By comparing the result of the calculation with experiment, the distribution of site reactivities in the real system can be approximated.

Reactivity distributions are presented in the form of histograms for three representative photopolymers. From these it can be seen that the photographic performance of the three systems is quite differently constituted. Thus, in poly(vinyl cinnamate) some 5% of all chromophore sites are responsible for the photosensitivity of the system, and these sites have very high reaction probabilities. By contrast, in the polyester of *p*-phenylenediacrylic acid the same initial quantum yield is achieved by a high proportion of moderately active chromophore sites. Finally, in the polymer based on diphenylpropene the high initial quantum yield of the triplet sensitized films must be attributed entirely to the high mobility of the excitation in the matrix.

The examples demonstrate that reactivity distributions provide a new insight into the molecular mechanism of some photoprocesses in the amorphous solid state. In the field of industrial photopolymers they are useful as a guide to further development. From a more general point of view, they are part of a fundamental understanding of the behavior of photoreactive amorphous solids.

Registry No. Poly(vinyl cinnamate), 24968-99-8; poly(vinyl alcohol) 1,2-diphenyl-3-cyclopropeneacetate, 83216-61-9; 1,4-bis(hydroxyethoxy)cyclohexane–3,3′-(*p*-phenylene)bis(acrylic acid) copolymer, 53710-66-0; 1,4-bis(hydroxyethoxy)cyclohexane-3,3′-(*p*-phenylene)bis(acrylic acid) (SRU), 58608-19-8.

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