Generation of Nonrandom Chromophore Distributions by the Photo-Fries Reaction of 2-Naphthyl Acetate in Poly(methyl methacrylate)

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ABSTRACT: The photochemical Fries reaction of 0.1–0.2 M 2-naphthyl acetate in glassy poly(methyl methacrylate) converts the naphthalene compound into products that act as long-range quenchers. Because each quencher suppresses formation of additional photoproducts in its immediate vicinity, the result is the formation of a nonrandom distribution of reactant donors and photoproduct quenchers, in which chromophores are more evenly distributed than in a truly random distribution. Singlet electronic energy migration and transfer within these nonrandom chromophore distributions were studied by steady-state fluorescence spectroscopy and fluorescence decay measurements. The donor fluorescence decays obtained for nonrandom distributions are clearly different from those predicted by models based on random chromophore distributions. Nonrandom distributions are converted to random distributions by solvent treatment or annealing for 4 days or more. The donor fluorescence decays of these new chromophore distributions correspond within experimental error to the predictions of the Förster and Loring–Andersen–Fayer models for energy trapping in random distributions.

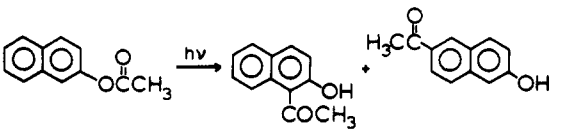
Introduction

Photodegradation, photooxidation, and photostabilization of polymers have developed into major branches of photochemistry during the past three decades.[1-5] Research in these areas has tended to focus on reaction mechanisms and product distributions, however, rather than on the differences between the kinetics of small-molecule and polymer photochemical reactions.

In most fluid solutions of small molecules, differences in chromophore environment at the instant of excitation are averaged out within the time scale of the excited-state lifetime by translational and rotational diffusion. This equivalence of chromophores leads to kinetic homogeneity and allows the description of photoprocesses in terms of rate constants. In solid polymers, however, such factors as slow diffusion, semicrystalline morphology, and stereochemical and sequence distribution effects may result in a highly inhomogeneous medium. Consequently, models of polymer degradation that are based on simple kinetic equations involving rate constants may give rise to serious errors in the interpretation of experimental results. Nevertheless, very few authors have called attention to the effects of kinetic and spatial inhomogeneity in polymer photodegradation.[6-8] As an isolated example Reiser and co-workers utilized a model involving distributions of quantum yields to interpret photo-cross-linking in solid polymers.[9] In a recent review Carlsson and Wiles stressed as well that the extension of classical kinetic schemes to solid polymers in the absence of diffusional mixing of reactants was open to contention.[7]

An area related to polymer photochemistry in which more attention has been devoted to kinetic inhomogeneity is the field of polymer photophysics, particularly in studies of long-range energy migration and transfer.[5,10-14] This is because the distribution of distances even between randomly distributed donors and quenchers in a solid polymer leads to complex kinetic behavior, which is described either by Förster kinetics in the limit of low donor concentration,[15,16] or by the model of Loring, Andersen, and Fayer at intermediate and high donor concentrations.[17] It is important to realize that both models are based on random distributions of both donors and traps, a situation that may not occur in all polymer photochemical systems of interest.

In the present paper we demonstrate that a fundamentally important photochemical reaction in polymers, namely the conversion of a reactant to a photoproduct that acts as a quencher, leads to nonrandom chromophore distributions and quenching behavior that is readily distinguished from that predicted by models based on random chromophore distributions. The system chosen was the photo-Fries reaction[18-21] of 2-naphthyl acetate donors in a glassy poly(methyl methacrylate) matrix (eq 1). In this system the photoreaction of a strongly



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fluorescent aromatic ester leads to the formation of nonfluorescent isomeric acetonaphthols that act as long-range singlet quenchers of the starting ester by the Förster mechanism. This system is similar to the poly(2-naphthyl methacrylate-*co*-methyl methacrylate) system investigated by us previously,[22] except that the use of the small-molecule chromophore allows variation of the donor concentration. As well, the current experimental work was conducted at considerably lower donor concentrations, so that the problem is primarily a fluorescence quenching process, and not one of electronic energy migration within the donor population.

Experimental Section

Materials. 2-Naphthyl acetate (Aldrich) was first distilled under high vacuum in a Kugelrohr apparatus, then treated with activated charcoal in hexane solution, and filtered. Large crystals with mp 69–70 °C were obtained after three recrystallizations from hexane. The ^1H and ^{13}C NMR spectra (Bruker AM-250) and the fluorescence spectrum of this ester showed no traces of

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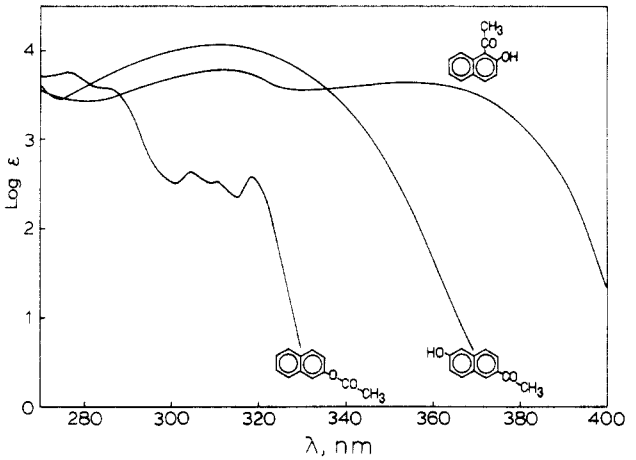


Figure 1. UV absorption spectra of 2-naphthyl acetate, 6-aceto-2-naphthol, and 1-aceto-2-naphthol in ethyl acetate.

Table I
Molar Extinction Coefficients at Representative Wavelengths for Naphthalene Compounds in Ethyl Acetate

	ε, M^{-1} cm^{-1}		
compd	312 nm	318 nm	357 nm
2-naphthyl acetate	307	389	0
1-aceto-2-naphthol	5930	5380	4390
6-aceto-2-naphthol	11700	10200	103

impurities. The compound was stored in the dark at −5 °C. 1-Aceto-2-naphthol and 6-aceto-2-naphthol were available from a previous study.[21] Poly(methyl methacrylate) was purchased from Polysciences; the sample had a weight-average molecular weight of 443 000 and a polydispersity of 2.66. THF (Caledon Laboratories, HPLC grade) was refluxed with CuCl, then distilled from $LiAlH_4$, and stored under nitrogen. Toluene (BDH Photrex grade) was used without further purification.

Film Preparation.[22,23] PMMA films containing homogeneously distributed 2-naphthyl acetate at a level of 1–2 wt % were prepared by solution casting from toluene or THF on 22-mm-diameter Suprasil disks (Hellma). The solvents were allowed to evaporate slowly under Pyrex watch glasses, and then the films were dried under high vacuum and examined by fluorescence spectroscopy. For thicker films repeated casting was carried out by using stock solutions of the same concentration as for the thinner films. Typical film thicknesses were 10–20 μm, measured by UV spectroscopy.

Irradiation Techniques.[22] The supported polymer films were positioned in a quartz container, which was evacuated and flushed three times with nitrogen. The container was transferred to a Rayonet Model RPR-100 photoreactor and irradiated with 280–320-nm light from 16 3000-Å lamps for the desired time. Figure 1 compares the UV absorption spectra of 2-naphthyl acetate and its isomeric photo-Fries products in ethyl acetate solution. Table I lists the molar extinction coefficients of the three compounds in ethyl acetate at representative wavelengths. From the measured absorbances at 312, 318, and 357 nm the concentrations of starting material and photo-Fries products in the film were calculated as a function of irradiation time by solving a set of three simultaneous linear equations. The degree of conversion of the starting ester is then $x = ([NA]_0 - [NA]_t)/[NA]_0$, where $[NA]_0$ and $[NA]_t$ represent the 2-naphthyl acetate concentrations at irradiation times 0 and t, respectively.

Spectroscopic Techniques. A Varian DMS UV–visible spectrophotometer was used for UV absorption measurements on both solutions and polymer films. Fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter. Spectra of films were measured with front-face viewing at an angle of 30°. Emission spectra were recorded under identical conditions with 287-nm excitation, the wavelength of the maximum of the excitation spectrum.

Fluorescence decay curves were recorded by the single-photon-counting technique using a PRA System 2000 instrument.[24] Polymer films on quartz were adjusted on an x–y–z–θ stage with front-face excitation. In order to obtain fluorescence decays free from scattered light, the polymer films were positioned at an angle of ca. 30° with respect to the excitation beam and were kept free from contaminants such as oil and dust, as well as prior exposure to UV light. After the instrument was adjusted with a test film or a clean quartz disk, samples were excited at 285 nm through a monochromator and emission at 335 nm was detected at a right angle through a second monochromator. It was occasionally necessary to add a Corion 340 band-pass filter or a Schott WG-335 cut-off filter or both to eliminate scattered excitation as completely as possible. The instrument response function was obtained at 335 nm by recording the scattered light from a pure poly(methyl methacrylate) film on quartz under the same conditions as were used to record the fluorescence decay. Fluorescence decays were analyzed by iterative reconvolution using mono-, bi-, and triexponential fitting functions, as well as the energy-transfer function (eq 2) derived by Förster for long-range dipole–dipole energy transfer in homogeneous solution:[16]

$$I_F(t) = \exp[-2\gamma(t/\tau_D)^{1/2}] \exp(-t/\tau_D) \quad (2)$$

where $\gamma = C/C_0$, with C_0 the Förster concentration, and τ_D is the lifetime of the donor in the absence of quenchers.[22] As well, a model developed by Loring, Andersen, and Fayer[17] was used to generate donor decay curves, allowing for the additional possibility of a small amount of donor–donor energy transfer via the Förster mechanism. Details of this computer calculation are found in an earlier publication.[22] Simulated decay curves were reconvoluted with an experimental instrument response function and normalized to the same area as the experimental decay curves. The two curves were then subjected to standard statistical tests for goodness of fit, including calculation of reduced χ^2, plots of weighted residuals, and evaluation of the autocorrelation function of the weighted residuals.[24] Experimental decay curves obtained for random chromophore distributions were allowed to shift by up to 0.5 channels (0.1 ns) relative to the instrument response function in order to correct for small differences in photomultiplier response between 285 and 335 nm.[24] No such time shift was allowed in the comparison of experimental decays obtained for nonrandom chromophore distributions with simulated decays obtained for random distributions. In these comparisons it was clear that the analysis program was treating the time shift as an extra fitting parameter to attempt to reconcile large differences between experimental and simulated decay curves and was thereby generating physically unrealistic time shifts of several data channels.

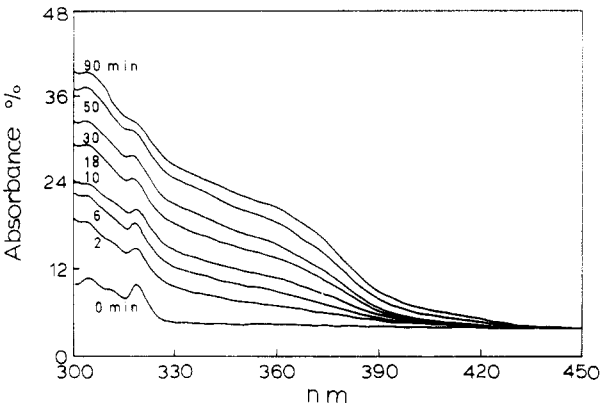


Figure 2. UV absorbance changes accompanying 280–320-nm irradiation of a poly(methyl methacrylate) film containing 0.172 M 2-naphthyl acetate.

Results and Discussion

On UV irradiation of thin films of poly(methyl methacrylate) containing low concentrations of 2-naphthyl acetate, a slow photo-Fries reaction proceeds that leads to the formation of a broad absorption band in the 300–400-nm range. Figure 2 shows typical absorbance changes accompanying 280–320-nm irradiation of 0.172 M 2-naph-

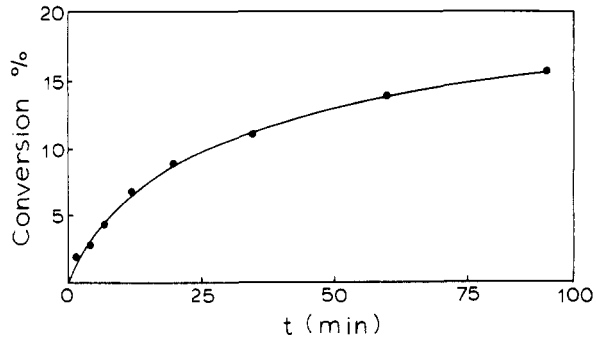
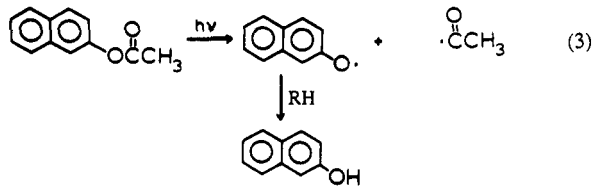


Figure 3. Variation of extent of conversion with time of 280–320-nm irradiation of a poly(methyl methacrylate) film containing 0.115 M 2-naphthyl acetate.

thyl acetate in PMMA. Similar behavior is observed for films cast from THF and toluene. The photoreaction appears to occur more slowly with increasing irradiation time, as is shown clearly by the conversion–time graph of Figure 3. For the particular film of the experiment shown in Figure 3 the photoreaction rate becomes negligible after ca. 15% conversion. This limiting conversion is concentration dependent. In much more dilute solutions of 2-naphthyl acetate the conversion–time curves are almost linear, while in more concentrated films the conversion–time curves level off at lower extents of conversion but at about the same molar concentration of photo-Fries products. This behavior is expected for a photoproduct acting as a long-range quencher of the excited singlet state of the remaining 2-naphthyl acetate in the film.

It is interesting that the photoproduct absorbance can be accounted for quite well by the two photo-Fries products shown in eq 1, without the need to invoke 2-naphthol as a reaction product (eq 3). The reason that significant yields



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of 2-naphthol are observed in the photoreaction in small-molecule solution but not in PMMA is probably the much greater magnitude of the cage effect in the glassy polymer matrix, which prevents formation of free 2-naphthoxy radicals capable of H-atom abstraction to yield 2-naphthol. Nor is there any evidence to support the existence of long-lived 2-naphthoxy radicals trapped in the PMMA matrix. Such a species would have an absorption spectrum in the visible,[25] which is not observed. Furthermore, dissolution of the irradiated film in toluene and recasting would remove the absorption spectrum of the radicals and restore the fluorescence of the unreacted 2-naphthyl acetate. In fact, the absorption spectrum of the film is unchanged by this procedure, and the donor fluorescence intensity increases only moderately.

Steady-state fluorescence measurements on PMMA films containing 2-naphthyl acetate, performed at different extents of conversion to photo-Fries products, provide additional evidence for long-range quenching. Typical results are shown in Figure 4. As the extent of conversion to photo-Fries products increases, the intensity of the fluorescence of the unconverted 2-naphthyl acetate decreases, but no new emission bands are observed. The degree of quenching of the fluorescence of the unreacted ester is far greater than the extent of conversion to acyl-

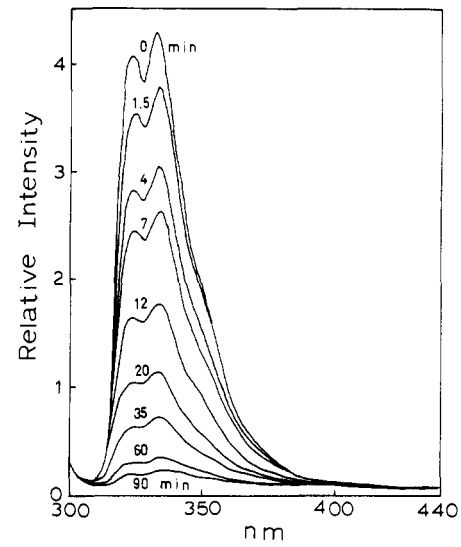

Figure 4. Variation of fluorescence intensity with time of irradiation at 280–320 nm for 0.115 M 2-naphthyl acetate dispersed in poly(methyl methacrylate) film.

naphthol products, a situation that cannot arise if the photoproducts function merely as screening agents. A simple analysis establishes that for a product acting as a competing absorber, the maximum reduction $\Delta I/I_0$ in the fluorescence intensity of the reactant is given by eq 4

$$\frac{\Delta I}{I_0} = 1 - \frac{(1-p)\epsilon_1}{(1-p)\epsilon_1 + p\epsilon_2} \tag{4}$$

where p is the degree of conversion, ϵ is the extinction coefficient at the excitation wavelength, and the subscripts 1 and 2 refer to starting ester and photo-Fries product, respectively. For $\epsilon_1 \cong \epsilon_2$ as in the present situation, the maximum reduction in fluorescence intensity at degree of conversion p is on the order of p itself, or ca. 15%. Furthermore, this maximum reduction would only be achieved for very thick films in which all of the incident light is absorbed. Reductions in fluorescence intensity on the order of 95% or greater for $p \cong 0.15$, as in the case of the data presented in Figure 4, can therefore only result from excited-state quenching and not from competing absorption.

Fluorescence decay measurements allowed us to go beyond the level of detail obtainable with steady-state fluorescence measurements and uncover significant differences between the 2-naphthyl acetate/photo-Fries product system and classical Förster energy-transfer systems. Since only the starting ester fluoresces in this experiment (Figure 4), the photo-Fries products must influence the decay behavior of the sample by long-range fluorescence quenching. Carefully purified 2-naphthyl acetate alone in poly(methyl methacrylate) films gave single-exponential decay with a lifetime of ca. 23 ns, as shown by the decay curve of Figure 5 and the compilation of results in Table II. The conversion to photo-Fries products by the flashlamp itself was sufficiently large during data acquisition to more than 2×10^4 counts in the maximum channel that small deviations from pure single-exponential decay were detected, usually in the form of higher than normal values of χ_R^2, as shown for example in Figure 5. The observation of exponential decay for 2-naphthyl acetate in the absence of photo-Fries products is also important, because it establishes that the effects of fluorescence depolarization, whether by energy migration, rotational diffusion, or the particular optical configuration of our instrument on the measured

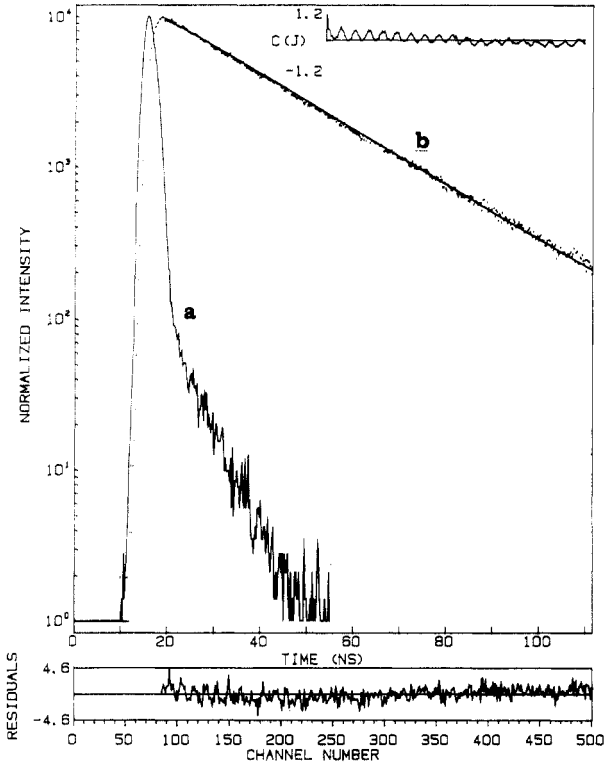

Figure 5. Fluorescence decay of 0.115 M 2-naphthyl acetate in a PMMA film cast from toluene; λ_{ex} = 285 nm, λ_{em} = 335 nm. Curve a is the instrument response function at 335 nm; Curve b points, experimental data; solid line, best-fit reconvolution with instrument response function. The reduced χ^2 is 1.52.

Table II
Fluorescence Lifetimes τ_D of 2-Naphthyl Acetate Dispersed in Poly(methyl methacrylate) Films

casting solvent	solute concn, M	τ_D, ns	χ_R^2
toluene	0.115	23.24	1.52
toluene	0.159	22.38	1.28
THF	0.172	22.59	1.43

fluorescence decays, are all negligible. Moreover, these exponential donor fluorescence decays, coupled with the high values of fluorescence polarization characteristic of isolated 2-naphthyl acetate molecules,[22] the complete absence of excimer fluorescence up to 2-naphthyl acetate concentrations 50 times higher than in the present work, and the almost exact match of the solubility parameters of 2-naphthyl acetate (9.3 ± 0.1) and PMMA (9.3),[26] establish that the initial solution of 2-naphthyl acetate in PMMA is random.

The fluorescence decay curves of the same film as in Figure 5, obtained following irradiation in a photoreactor for various lengths of time, are no longer exponential. Furthermore, as the collection of decay curves in Figure 6 illustrates, the deviation from exponential decay increases with increasing conversion to photo-Fries products. One way of expressing these in a way that is independent of quenching mechanism is to determine the mean lifetime of fluorescence.[27] If all of the decay curves of Figure 6 can be represented adequately by triple-exponential decay curves (eq 5)

$$I_F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \quad (5)$$

then the mean lifetime $\langle\tau\rangle$ of each decay curve is given

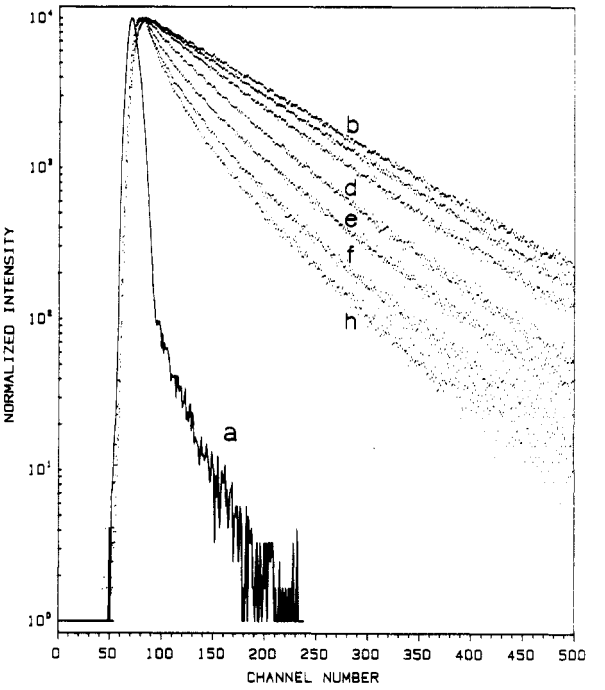

Figure 6. Variation of the fluorescence decay of 0.115 M 2-naphthyl acetate in PMMA film cast from toluene with extent of irradiation at 280–320 nm. λ_{ex} = 285 nm; λ_{em} = 335 nm; (a) instrument response function. Irradiation times are (b) 0, (c) 1.5, (d) 7, (e) 12, (f) 35, (g) 60, and (h) 90 min.

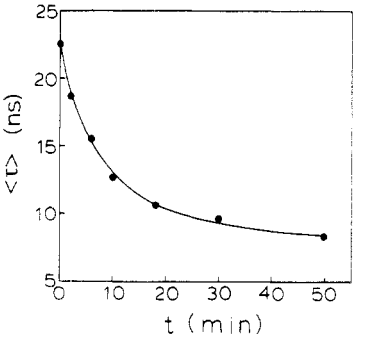

Figure 7. Variation of the mean fluorescence lifetime $\langle\tau\rangle$, defined in eq 6, with extent of irradiation at 280–320 nm for 0.172 M 2-naphthyl acetate in PMMA.

by

$$\langle\tau\rangle = \frac{\int_0^\infty tI_F(t)\,dt}{\int_0^\infty I_F(t)\,dt} = (\sum_{i=1}^{3} A_i\tau_i^2)/(\sum_{i=1}^{3} A_i\tau_i) \quad (6)$$

This mean lifetime represents a qualitative measure of change in the sample composition but was not used as a parameter in any energy-transfer model. Figure 7 shows the variation of $\langle\tau\rangle$ with irradiation time for 2-naphthyl acetate in PMMA prepared by casting from THF solution, the same sample as in entry 3 of Table II. The decrease in $\langle\tau\rangle$, followed by a leveling off at long irradiation time, mirrors the change in the extent of conversion to photo-Fries products with irradiation time shown in Figure 3. This is additional evidence that once quenching by the photo-Fries products becomes sufficiently fast, further conversion becomes increasingly difficult.

If partially reacted 2-naphthyl acetate in glassy PMMA is treated with a small amount of toluene and the solvent is then evaporated or if the films are simply allowed to stand at room temperature for a week or more, then the donor fluorescence decays show significant changes. The mean lifetimes of these new decays are all longer than for

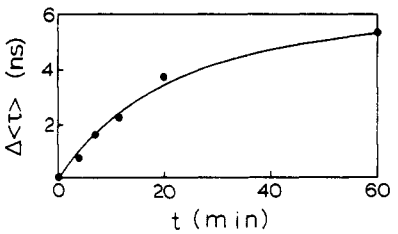

Figure 8. Variation of difference $\Delta\langle\tau\rangle$ in mean donor fluorescence lifetime immediately after irradiation and after conversion to random distributions by treatment with toluene for 0.115 M 2-naphthyl acetate films in PMMA.

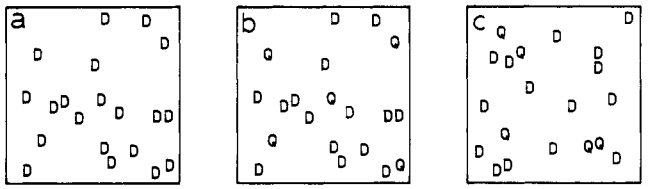

Figure 9. Nonrandom and random chromophore distributions in the photochemistry of 2-naphthyl acetate in PMMA matrices: (a) random distributions of 2-naphthyl acetate donors D before irradiation; (b) generation of nonrandom donor and quencher Q distributions during photo-Fries reaction; (c) restoration of random chromophore distributions by annealing or treatment with toluene.

decays obtained immediately after irradiation, and the increase in mean lifetime $\Delta\langle\tau\rangle$ increases with the extent of conversion, as shown in Figure 8.

A conceptual illustration of the effects of solvent treatment or prolonged annealing on the donor fluorescence decays is shown in Figure 9. During the course of the photo-Fries reaction each new quencher Q tends to prevent the formation of further photo-Fries products within a sphere of radius R_{DQ} around the quencher. The result is a nonrandom distribution of both donors and quenchers in which there is a reduced tendency for the quenching domains to overlap, as shown in Figure 9b. When the chromophores are allowed to diffuse as a result of softening of the matrix by absorption of toluene or by long standing, then the random chromophore distributions are restored. In this random distribution, shown in Figure 9c, the normal statistical overlap of quenching domains is once more present.

An alternative model for the effects of solvent treatment and annealing on donor fluorescence decays was considered and rejected. In this model it was proposed that there might be a large gradation of quencher concentrations from the outside to the inside of the film as a result of the high absorbance of the film. The fluorescence from the donor population might therefore be heterogeneous since it would be a superposition of decays from regions with higher and lower concentrations of quencher. The way the experiment was performed tends to reduce this effect. The high-intensity irradiation of the films to generate photo-Fries products was performed with polychromatic light with a maximum intensity between 300 and 310 nm. At these wavelengths the absorption of 2-naphthyl acetate is low ($\epsilon < 500\ M^{-1}\ cm^{-1}$), and the attenuation of the light passing through the sample is small, as is evident from inspection of Figures 1 and 2. In contrast, the fluorescence decays were measured with excitation at 285 nm, where the absorbance is much greater ($\epsilon \cong 4000\ M^{-1}\ cm^{-1}$). Thus the depth of penetration of the light into the film is much shallower, and the fluorescence decay measurement interrogates a much smaller range of donor/quencher concentrations than is actually present in the film. Moreover, it is unlikely in such a mechanism that merely allowing the film to stand for a week would restore the same random distributions of donor and quencher attained by treating the film with solvent. Diffusion of chromophores such as 2-naphthyl acetate and its photo-Fries product, which are large relative to the size of the repeating units in PMMA, over distances on the order of $R_{DQ} = 2$ nm, the Förster radius for quenching, may occur on such a time scale in glassy PMMA. On the other hand, diffusion over distances of the film thickness, which was 10–20 μm, would require several years, in view of upper bounds on diffusion coefficients of $10^{-16}\ cm^2\ s^{-1}$ for molecules of similar size in PMMA.[28]

Finally, a third reason for rejecting the concentration gradient model arises from the very strongly autoinhibiting nature of the photoreaction, as revealed by the conversion–time plot of Figure 3. If there is a higher conversion to photo-Fries products on the outer surface of the film as a result of high sample absorbance, then further conversion in this region becomes increasingly difficult because of quenching by the photoproducts. As a result the extent of conversion within the film interior is able to catch up.

The following is a typical experiment that serves to establish the time scale for evolution from the nonrandom to the random chromophore distribution in glassy PMMA films of 2-naphthyl acetate. A particular film was irradiated for 10 min at 280–320 nm and then allowed to stand for 4 days at room temperature. At this point the mean fluorescence lifetime $\langle\tau\rangle$ had increased from a value on the order of 17.60 ns immediately after irradiation to 19.85 ns. The film appeared to have reached a random chromophore distribution during this time, as subsequent treatment with toluene and redrying produced no further increase in $\langle\tau\rangle$. In fact, the mean lifetime after solvent treatment decreased slightly to 19.34 ns, possibly as a result of the formation of a small degree of additional photo-Fries products by the flashlamp during the first fluorescence decay measurement. From experiments such as this we arrive at an upper limit of 4 days for evolution from the nonrandom to the random chromophore distribution at room temperature.

Comparison with Random Models. The fluorescence decay data obtained for different degrees of conversion to photo-Fries products were analyzed by using two models of long-range quenching derived for diffusionless random systems. These were the Förster kinetic model,[16] which describes dipole–dipole transfer between randomly distributed donors and quenchers, and the Loring–Andersen–Fayer (LAF) model,[17] which allows for both donor–donor and donor–quencher excitation energy transfer in random systems. At the low donor concentrations used in our experiments the two models generate almost identical decay curves, because the extent of donor–donor transfer is very small.

Figure 10 illustrates the excellent agreement achieved between the predictions of the LAF model and typical experimental fluorescence decay curves obtained for random chromophore distributions. The deviation between experimental and best-fit calculated decay curves in Figure 10 is everywhere within 3.5 standard deviations and there are no systematic deviations between the curves other than those produced by a trace of rf noise superimposed on the experimental curves. The best-fit values of the reduced donor and quencher concentrations C_D and C_Q are physically meaningful and correspond closely to those determined from UV absorbance measurements. Table III lists typical values of χ_R^2, the reduced χ^2, for analysis of fluorescence decay data obtained for random chromophore distributions for a wide range of extents of

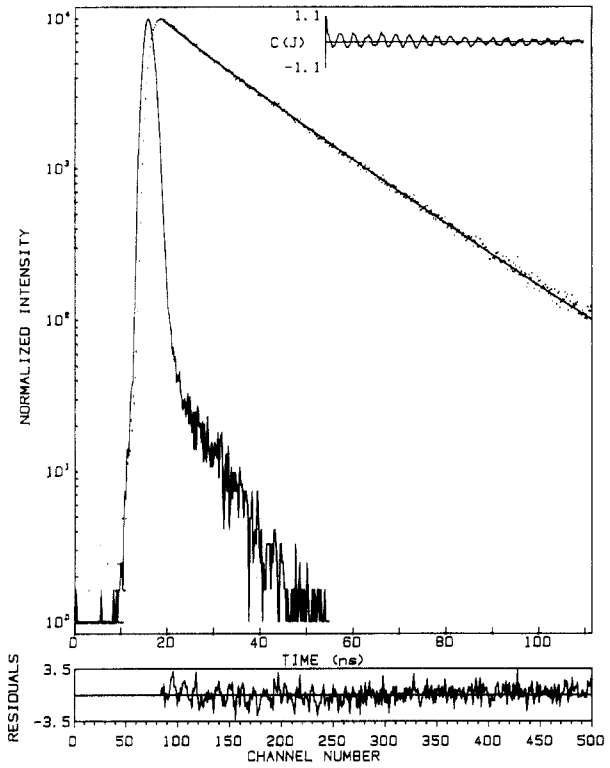

Figure 10. Analysis of fluorescence decay curves by a model erived for random donor and quencher distributions. Points: experimental fluorescence decay curve for 0.115 M 2-naphthyl acetate in PMMA after 12 min of UV irradiation and conversion to a random chromophore distribution by solvent treatment and drying. Smooth curve: best-fit decay calculated from Loring–Andersen–Fayer model and reconvoluted with an experimental lamp profile. The reduced donor and quencher concentrations are 0.10 and 0.23, respectively. $\chi_R^2 = 1.37$.

Table III
Comparison of Reduced χ^2 Values for Analysis of Fluorescence Decays of 2-Naphthyl Acetate in PMMA by Random Quenching Models

	χ_R^2(Förster model)		χ_R^2(LAF model)	
UV irrad time, min	nonrandom distrib[a]	random distrib[b]	nonrandom distrib[a]	random distrib[b]
0		1.61		1.55
4	3.65	1.75	2.95	1.74
7	3.06	1.83	2.59	1.52
12	2.50	1.45	2.12	1.37
20	5.02	1.65	4.42	1.45
>30	12.40	1.74	11.20	1.58
60	12.54	1.57	15.31	1.69
90	15.53	1.82	17.77	1.47

[a] Obtained immediately after irradiation. [b] Obtained after treatment of the film with toluene and redrying.

conversion to photo-Fries products. The ability of both Förster and LAF models to describe fluorescence quenching accurately in random systems is evident as shown by χ_R^2 values between 1.37 and 1.83 for all degrees of conversion.

In marked contrast to these well-behaved random distributions, the nonrandom distributions generate fluorescence decays that can be fit only very poorly by the Förster and LAF quenching models. Values of χ_R^2 for typical analyses, listed in Table III, are much larger than those obtained for random distributions. Furthermore, the values of C_D and C_Q used to generate these best-fit decays are now spurious, bearing little relationship to the spectroscopically determined concentrations. The mathematical analysis merely succeeds in finding values of C_D and C_Q that fit the region around the maximum of the decay curve, where the contribution to the overall χ_R^2 is greatest. Away from the decay maximum the calculated curve wanders away from the experimental decay by many standard deviations. The analyses summarized in Table III establish that the fluorescence decays for nonrandom and random chromophore distributions are clearly differentiable and that the differences between the two increase with increasing conversion of donors to quenchers.

Conclusions

The conversion of 2-naphthyl acetate into its photoproducts by a gradual photoreaction in a polymer matrix can be regarded as a prototype for polymer photodegradation. We have shown that under diffusion-free conditions, such as exist in glassy poly(methyl methacrylate), a product that functions as a long-range quencher generates an unusual nonrandom chromophore distribution as the photoreaction proceeds. In this distribution quencher chromophores are somewhat more evenly spaced than in a random distribution. The existence of this nonrandom distribution was clearly demonstrated by studies on the fluorescence decay of the donor population. The effect is manifested as a complete failure of models derived for random distributions to reproduce the fluorescence decays obtained immediately after irradiation, even though these models were completely capable of describing the fluorescence decays once the chromophore distributions had been made random by solvent treatment or annealing.

This nonrandom chromophore distribution has some intriguing properties. The efficiency of quenching of the donor population is greater for the nonrandom distribution than it is for the same quencher concentration in a random distribution, because there is less overlap of the spheres of influence of different quenchers. Starting from a random donor population, the system becomes increasingly nonrandom as more donors are converted to quenchers. On the other hand, if one could imagine conversion of nearly all the donors to quenchers as a result of extremely long irradiation times, the nonrandom quencher distribution should evolve back to a random one. This property, together with the fact that such a distribution can be erased instantly by solvents or even gradually by annealing, makes it remarkably elusive! Nevertheless by working in a carefully selected donor concentration range where the effect was greatest, we have been able to study the properties of this distribution.

The next step in this research is the development of a model that allows generation of nonrandom chromophore distributions and the modeling of energy migration and transfer within them. Details of a full Monte Carlo simulation of both processes will be published separately.[29]

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Liquid-Crystalline Polymer Gels. 1. Cross-Linking of Poly(γ-benzyl L-glutamate) in the Cholesteric Liquid-Crystalline State

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ABSTRACT: Cross-linking of poly(γ-benzyl L-glutamate) in the cholesteric liquid-crystalline (CLC) state was carried out by using several diamines of different chain types as the cross-linkers in three different solvents. A PBLG/triethylenetetramine/dioxane mixture was found to be the best system, which upon heating at 70 °C for about 10 days gives a polymer gel, keeping the original cholesteric order. The cholesteric order disappeared when the gel was immersed in dichloroacetic acid, but the original CLC order was reproduced by immersing the gel again in dioxane. Therefore, the CLC structure was found to be memorized in the cross-linking networks. The reversible transition was induced also by the temperature change.

Cross-linked gels of synthetic polymers are usually isotropic and show no microscopic and macroscopic order. Gels with mechanical and optical anisotropy will be new materials that may find applications in a variety of fields. One of the promising approaches to the anisotropic gel is the cross-linking of lyotropic liquid-crystalline (LLC) polymers. If one can cross-link the LLC polymers without disturbing the original LC order and if the cross-linked polymer has the typical properties of a gel, a highly anisotropic polymer gel, which may be called a "liquid-crystalline (LC) gel", will be obtained.

Poly(γ-benzyl L-glutamate) (PBLG) forms a cholesteric LC (CLC) in a concentrated solution in chloroform, methylene dichloride, dioxane, and so on.[1,2] Aviram[3] reported the cross-linking of PBLG with 1,6-diaminohexane in chloroform and obtained an anisotropic material. However, he did not report the gel property of the cross-linked PBLG. Moreover, it was found in our experiment that the reaction mixture became heterogeneous under his condition and no gelation occurred even after 20 days at 70 °C. In this paper, the cross-linking was examined by using diamines with different chain types in three different solvents. Under the optimum condition found in this study, PBLG was cross-linked smoothly and the resulting gel showed the original cholesteric order.

The immobilization of the CLC structure of PBLG has been attempted by γ-ray irradiation of a dry film of PBLG or a film of PBLG/plasticizer mixture.[4] A mixture of poly(glutamic acid) and poly(ethylene glycol) in dimethylformamide was cast to form a film possessing the CLC order.[5] In this case the CLC order has been stabilized not by covalent bonds but by hydrogen bond networks. The CLC structure of a concentrated polypeptide solution in a vinyl monomer as a solvent was fixed by polymerizing the vinyl monomer in the presence of a small amount of divinyl monomer as a cross-linker.[6,7] However, these studies are not aimed to prepare a gel with the cholesteric order.

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