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# Studies of Polymer Photostabilization Using Fluorescence Spectroscopy: Photochemistry of Naphthyl Methacrylate Copolymers

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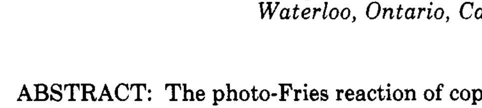
ABSTRACT: The photo-Fries reaction of copolymers of minor amounts of 1- and 2-naphthyl methacrylate (NMA) with styrene and methyl methacrylate was investigated in the solid state. Slow growth of photoproduct absorbance is accompanied by a rapid decrease in the fluorescence intensity of the unreacted naphthyl ester groups. Conversion of NMA to copolymerized acylnaphthols occurs by the photo-Fries reaction until the products suppress further photoreaction. Measurement of the fluorescence decays of the unreacted NMA units established that fluorescence quenching occurs by Förster transfer to the photoproducts over a range of 2.6 ± 0.1 nm. Only a minor role is played by electronic energy migration in this quenching because of the low NMA concentration in the copolymer films. The decays of the donor fluorescence at different extents of conversion to photo-Fries products were analyzed by the model of Loring, Andersen, and Fayer, which describes energy migration and Förster transfer in homogeneous diffusion-free solution. This model correctly predicted the donor fluorescence response function at all but the shortest times following excitation. The suggestion is made that small deviations from the predictions of the Fayer model may arise because the distribution of quenchers produced by the solid-state photo-Fries reaction is not perfectly homogeneous.

## Introduction

Photoreactions occurring in commercial plastics frequently have adverse effects. Photodegradation and photooxidation may lead to yellowing and loss of mechanical strength, either through softening or through embrittlement.[1] The photo-Fries reaction[2] of aromatic esters and amides, shown in eq 1, is frequently a troublesome photoreaction in solid polymers. It builds up products which are themselves capable of further photoreaction, even though the primary photoreaction does not lead directly to chain scission. Among polymers susceptible to discoloration by the photo-Fries reaction are bisphenol A polycarbonate,[3,4] aromatic polyamides,[5] poly(phenyl acrylate),[6,7] and the poly(naphthyl acrylates) and poly(naphthyl methacrylates).[8,9]



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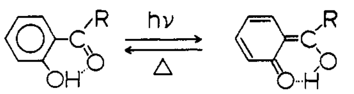
In the case of phenyl esters the *o*-hydroxyphenone photoproduct has a reduced tendency toward further reaction because its excited singlet state is rapidly deactivated by intramolecular H-atom abstraction, followed by enolization to the ground-state starting material (eq 2).



(2)

This deactivation pathway is not available to the para isomer, which retains a significant quantum yield of photoreaction in nonpolar solvents.[2] In the case of the poly(naphthyl methacrylates) the products are acylnaphthols having high extinction coefficients throughout the near-UV. In addition, their lowest triplet states have $\pi\pi^*$ character: the excitation resides predominantly on the aromatic ring and as a result the photoreactivity of the acylnaphthols, particularly in intermolecular hydrogen abstraction reactions, is much lower than that of the phenyl analogues. These acylnaphthols therefore fulfill two essential requirements for use as stabilizers against further photodegradation of the polymer.[10,11]

Almost all commercial photostabilizers are low molecular weight additives which are blended with polymers during processing.[12] Slow diffusion of these additives from the finished material is a problem and is offset at increased cost by the use of di- or trifunctional derivatives, often with long hydrocarbon chains to enhance solubility and reduce mobility. Such problems do not exist with the acylnaphthols derived from photolysis of naphthyl methacrylate residues because the photostabilizer is chemically attached to the polymer. The obvious advantages of polymer-bound photostabilizers have led to the synthesis and copolymerization of vinyl monomers incorporating stabilizing chromophores,[13-18] such as *o*-hydroxybenzophenone and (2-hydroxyphenyl)benzotriazole groups. The added synthetic complexity has tended to hinder commercial exploitation of this approach. In our case, since the bound stabilizers are generated from copolymers of naphthyl methacrylate, the number of synthetic steps is reduced considerably. The present publication describes the results of an investigation of the photo-Fries reaction of 1- and 2-naphthyl methacrylate (NMA) in copolymers with styrene and methyl methacrylate (MMA). This photoreaction is ideally suited for study by luminescence spectroscopy because it involves the conversion of a fluorescent starting material into a nonfluorescent product. Additional information is obtained through the fact that the product phosphoresces intensely at 77 K. Sophisticated fluorescence decay measurements have allowed us to determine the mechanism by which the photo-Fries products exert their stabilizing effect. These studies have important general implications in polymer photostabilization and also suggest techniques by which the effectiveness of UV stabilizers may be enhanced.

## Experimental Part

**General.** Infrared spectra were recorded on a Perkin-Elmer 457 instrument. $^1$H NMR spectra were measured on a Bruker WP-80 FT spectrometer with $Me_4Si$ as internal reference. A Cary 118 spectrometer was used for UV absorption measurements of both solutions and polymer films. Number-average molecular weights were determined with a Hewlett-Packard Model 502 membrane osmometer with toluene as solvent. Size exclusion chromatography of copolymers dissolved in toluene was performed on a Waters Model 590 instrument with a Model R401 differential refractometer detector.

**1-Naphthyl Methacrylate.** This monomer was prepared from the sodium salt of 1-naphthol and methacryloyl chloride following literature methods.[19,20] The crude product was distilled under

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high vacuum through a short insulated column to give an oil: $n^{20}{}_D$ 1.5943; IR (neat) 1730, 1630 cm$^{-1}$, NMR (CDCl$_3$) $\delta$ 2.15 (s with hyperfine splitting, 3 H), 5.84 (m, 1 H, 1.5-Hz coupling with the other vinylic proton), 6.51 (m, 1 H, 1.0-Hz coupling with the methyl protons), 7.23–7.93 (complex m, 7 H).

**2-Naphthyl Methacrylate.** A solution of 9.6 g of 2-naphthol and 5.9 g of dry pyridine in 100 mL of dry benzene was stirred at 0 °C while 7.0 g of distilled methacryloyl chloride was added over 1 h. Stirring was continued overnight and the solution was extracted with water, 1 M HCl, and dilute KOH solution and dried over Na$_2$SO$_4$. The filtered solution was treated with activated charcoal and refiltered. After evaporation of the solvent the monomer was sublimed twice under high vacuum at 40 °C. The product had the following properties: mp 62–64 °C; IR (Nujol) 1720, 1625 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 2.10 (partially resolved m, 3 H), 5.78 (partially resolved m, 1 H), 6.40 (partially resolved m, 1 H), 7.19–7.92 (complex m, 7 H).

Styrene and methyl methacrylate were washed with dilute aqueous NaOH to remove inhibitor, dried, and distilled at reduced pressure. Copolymers were prepared by free-radical polymerization of the monomers in degassed benzene at 50 °C, using 0.25 wt % AIBN as initiator. The polymers were precipitated from benzene into ethanol at about 30% conversion and were dried under high vacuum. The compositions of the copolymers were determined by UV spectroscopy, using the extinction coefficients of 1- and 2-naphthyl isobutyrate and homopolymers of 1- and 2-NMA as references.[8] (The general absence of marked changes in extinction coefficients in going from small-molecule naphthalene compounds to polymers has been discussed by Frank and Semerak.[21])

**Film Preparation.** Films were prepared by spin coating from toluene solution at 5000 rpm on 13-mm-diameter Suprasil disks (Hellma), using a Model EC 101D photoresist spinner (Headway Research, Garland, TX). Larger films were obtained by slow evaporation of toluene solutions on the surface of distilled water. In both cases the films were dried thoroughly over P$_4$O$_{10}$ under high vacuum.

**Irradiation Techniques.** Polymer films were irradiated in air in a Rayonet Model RPR-100 photoreactor with light from 16 3000-Å lamps. The air temperature was 35 °C. Changes in the absorption spectra were recorded against a quartz disk as reference. Light intensities were measured by 2-undecanone actinometry, with the yield of 1-octene formed by the Norrish Type II scission reaction determined by gas chromatography.[22,23] Typical measured light intensities in the range 290–320 nm were $5 \times 10^{-8}$ einstein cm$^{-2}$ s$^{-1}$.

**Fluorescence Techniques.** Fluorescence spectra were recorded with a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter. Spectra of films were measured with front-face viewing at an angle of 30°. Fluorescence polarization was measured as described in a preceding publication.[24] Phosphorescence spectra were recorded with a phosphorimeter constructed in the Faculty of Science shops, using techniques described elsewhere.[9]

Fluorescence decays were recorded by the single-photon-counting method using Photochemical Research Associates' System 2000 lifetime instrumentation. Polymer films on quartz disks were positioned with an $X$-$Y$-$Z$-$\theta$ stage. Samples were excited at 280 nm through a monochromator and emission was detected at 90° through a 337-nm interference filter (Corion).

Fluorescence decay curves were analyzed over at least a 100-fold range of intensity by the method of iterative reconvolution with a minimization of $\chi_R{}^2$, the reduced sum of squares of the residuals. FORTRAN-77 programs were run on an IBM-PCXT equipped with an 8087 floating-point coprocessor. Several trial functions were used to test whether the decay curves of the naphthalene fluorescence from photodegraded copolymers deviated from the behavior expected for one-step Förster transfer, but the most successful function was

$$I_f(t) = A_1 \exp[-(1/\tau_f + 1/A_2)t] \exp[-2A_3(t/\tau_f)^{1/2}] \qquad (3)$$

This equation represents the minimum extension of the Förster equation (eq 4), which was capable of fitting the experimental

$$I_f(t) = B_1 \exp(-t/\tau_f) \exp[-2B_2(t/\tau_f)^{1/2}] \qquad (4)$$

decay curves. In eq 3 and 4 $\tau_f$ is the fluorescence decay time of the copolymerized NMA in the absence of photodegradation. It was obtained for the unirradiated film and was fixed in subsequent analyses. The best-fit values of the parameters were obtained by using Marquardt's algorithm for gradient search.[25] The exp($t^{1/2}$) term in eq 3 prevents the use of the trapezoidal rule for convolution of the calculated decay curves with the lamp profile. This feature, together with the fact that the convergence of the parameters to their best-fit values is very slow, meant that it was frequently necessary to perform several hundred iterations, with a total computation time of 2–4 h.

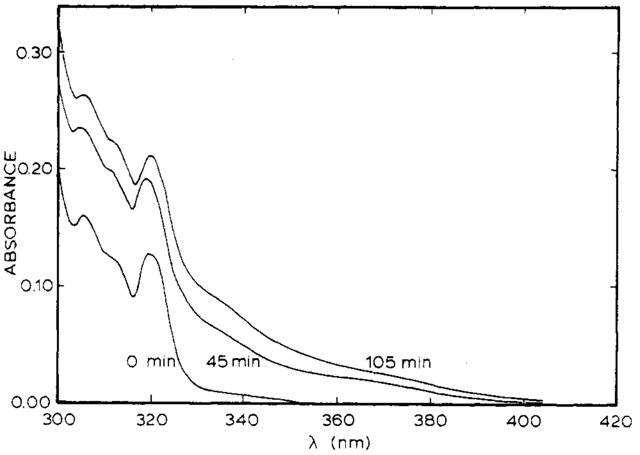

**Figure 1.** Absorbance changes accompanying 300-nm irradiation of a film of poly(styrene-*co*-4.7% 2NMA) on quartz.

Donor decay curves were also analyzed by using a model developed by Fayer and co-workers.[26,27] This model involves electronic energy migration between donor chromophores by sequential Förster transfers and Förster transfer to randomly distributed quenchers and predicts the dependence of the donor trapping function $G^D(t)$ on donor and quencher concentrations. The donor fluorescence decay for pulsed excitation is then given by

$$I_f(t) = G^D(t) \exp(-t/\tau_f) \qquad (5)$$

The Laplace transform $G^D(s)$ of the energy-transfer function was inverted numerically by the Stehfest method,[28] using double-precision arithmetic and 18 terms in the approximate expression for $G^D(t)$. To generate decay curves for comparison with experiment, the calculated points $G^D(t_i)$ were multiplied by the donor decay function measured in the absence of quenchers, then rounded to single precision, reconvoluted with an experimental instrument response function, and area-normalized over the analysis interval. Calculated and experimental decay curves were subjected to the normal statistical criteria for goodness of fit, including determination of $\chi_R{}^2$, point-by-point residuals, and the autocorrelation function of the residuals.

Förster radii for long-range energy transfer were calculated from absorption and emission spectra.[29-32] A small program in compiled Basic allowed spectra to be digitized from a Hewlett-Packard 7470A plotter and stored in a library on disk. The absorption spectra of various isomeric acetonaphthols were used to approximate the spectra of the polymer-bound photodegradation products. Details of the preparation and purification of these compounds and 2-naphthyl pivalate and acetate are found in an earlier publication.[8]

## Results and Discussion

Figure 1 shows the absorbance changes which accompany the irradiation of a poly(styrene-*co*-2-naphthyl methacrylate) film at 300 nm. A gradual increase of absorbance is observed in the region 320–400 nm. Similar absorbance changes occur on irradiation of poly(2-naphthyl methacrylate) and poly(2-naphthyl acrylate) in deoxygenated THF or benzene solutions.[8,9] Figure 2 shows the phosphorescence spectrum of the irradiated polymer obtained on excitation in the wavelength region where only the photoproducts absorb. The phosphorescence spectrum of 1-aceto-2-naphthol is shown for comparison. It is clear

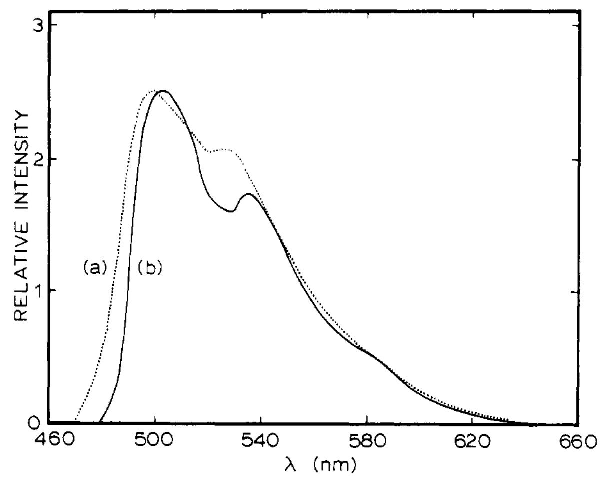

**Figure 2.** Phosphorescence spectra at 77 K of (a) irradiated poly(styrene-*co*-2NMA) film and (b) 4% 1-aceto-2-naphthol in polystyrene film. The excitation wavelength is 350 nm.

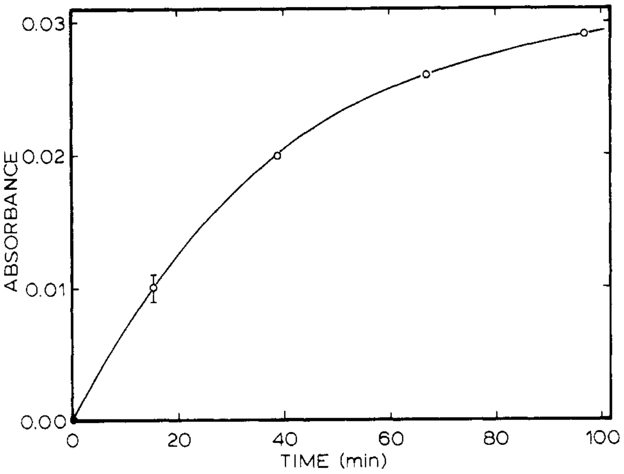

**Figure 3.** Growth of absorbance at 340 nm on 300-nm irradiation of a poly(methyl methacrylate-*co*-5.6% 2NMA) film on quartz.

that the origin of the long-wavelength absorption is the photo-Fries reaction of the naphthyl ester group, as shown in eq 6, and not the photodegradation of polystyrene.

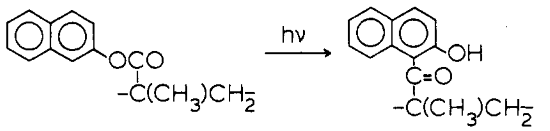

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Figure 3 illustrates the growth of absorbance at 340 nm during irradiation of a poly(methyl methacrylate-*co*-2NMA) film. The conversion–time curves are strongly curved and the photoreaction rate becomes negligible after only about 5% of the NMA groups have been converted to products. This behavior is in contrast to the almost constant quantum yield observed for the same photoreaction in poly(2NMA) in fluid solution.[8]

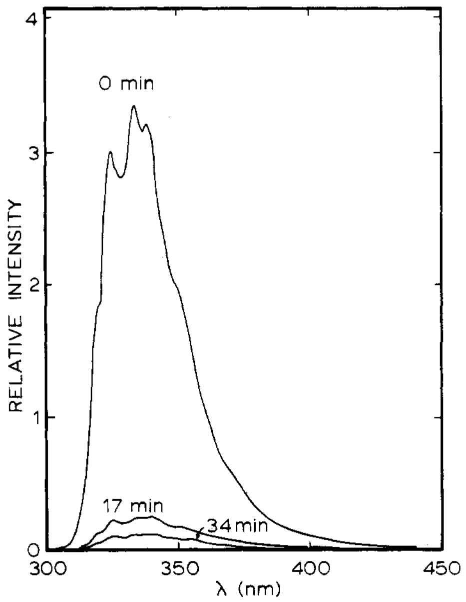

**Figure 4.** Change in the fluorescence spectrum of a poly(MMA-*co*-4.5% 1NMA) film with time of 300-nm irradiation in air.

**Table I**
**Properties of NMA Copolymers**

| sample | monomer 1 | monomer 2 | mol % NMA in copolymer | $M_n \times 10^{-5}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | styrene | 1NMA | 7.5 | 1.06 | 2.07 |
| 2 | MMA | 1NMA | 4.5 | 4.3 | *a* |
| 3 | styrene | 2NMA | 4.7 | 1.04 | 3.03 |
| 4 | MMA | 2NMA | 5.6 | 2.1 | *a* |

[a] Composition varies with molecular weight so that SEC results are invalid.

**Table II**
**Förster Radii $R_0$ and Concentrations $C_0$ for Long-Range Singlet Energy Transfer from Copolymerized Naphthyl Methacrylates to Various Acceptors**

| donor | acceptor | $R_0$, nm | $C_0$, M |
|---|---|---|---|
| 1NMA | 2-aceto-1-naphthol | 2.46 | 0.030 |
| 1NMA | 4-aceto-1-naphthol | 2.69 | 0.023 |
| 1NMA | 1-aceto-2-naphthol | 2.48 | 0.029 |
| 1NMA | 6-aceto-2-naphthol | 2.55 | 0.027 |
| 2NMA | 2-aceto-1-naphthol | 2.46 | 0.030 |
| 2NMA | 4-aceto-1-naphthol | 2.70 | 0.023 |
| 2NMA | 1-aceto-2-naphthol | 2.49 | 0.029 |
| 2NMA | 6-aceto-2-naphthol | 2.55 | 0.027 |
| 1NMA | 1NMA | 1.09 | 0.345 |
| 2NMA | 2NMA | 1.12 | 0.318 |
| polystyrene excimer | 1NMA | 1.79 | 0.078 |
| polystyrene excimer | 2NMA | 1.58 | 0.113 |

Fluorescence spectroscopy of the copolymer films provides insight into the observed conversion–time behavior. The concentration of naphthalene chromophores in a film of a copolymer containing 5% NMA is approximately 0.5 M. At this concentration the fluorescence spectrum of the styrene–NMA copolymers displays only emission from the naphthalene chromophore, even on excitation at the absorption maximum of the phenyl chromophore. The excited monomer and excimer states of polystyrene are quenched quantitatively by energy transfer to copolymerized NMA. Figure 4 illustrates typical changes in the fluorescence spectrum of the naphthyl ester chromophore accompanying irradiation of copolymer films. A pronounced decrease in the NMA fluorescence intensity is observed during irradiation and is out of all proportion to the actual conversion of NMA to photo-Fries products. The absorbance of the photoproducts at the irradiation wavelength is 2 orders of magnitude too small for this decrease in fluorescence intensity to correspond to competing absorption. It is apparent that the photo-Fries products quench the excited singlet state of NMA with high efficiency.

The irradiated films remain completely soluble in THF up to irradiation times of 1 h. When a film irradiated to its limiting conversion is dissolved in THF, the strong fluorescence of the unreacted NMA is recovered. This result indicates that the quenching efficiency of the pho-

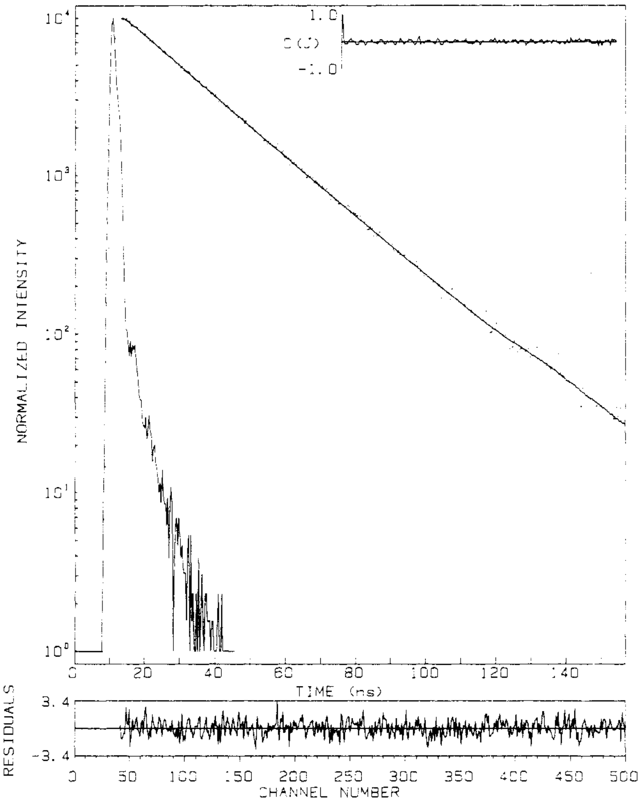

**Figure 5.** Fluorescence decay of poly(MMA-2NMA) film on quartz before photodegradation. Solid line: lamp profile; points: decay at 337 nm. Coinciding with the decay data points is the convolution of the best-fit double-exponential decay law with the lamp profile: $I_f(t) = 0.2258 \exp(-t/14.98 \text{ ns}) + 0.7742 \exp(-t/23.97 \text{ ns})$. Under the decay curves of Figures 5–7 are the plots of the weighted residuals for each decay channel. The insets at the top right of each decay curve show the autocorrelation function $C(J)$ of the residuals.

toproducts arises from the high local concentration of quencher in the copolymer films. Table II lists values of the Förster radii for Coulombic energy transfer from copolymerized NMA to various acetonaphthols, calculated from spectroscopic data. These interaction distances are typically 2.6 nm and correspond to Förster concentrations $C_0$, corresponding to 72% energy transfer, of 0.026 ± 0.004 M. Thus at a bulk naphthalene concentration of 0.5 M, only about 5% conversion of NMA units to photo-Fries products would be sufficient to quench further photoreaction. This is close to the limiting conversion observed experimentally. When the quencher is diluted by dissolution of the polymer, the unreacted NMA units are again capable of fluorescence. If the irradiated polymer is purified by reprecipitation and a film is subsequently prepared by solution casting on quartz, the fluorescence intensity is once more reduced. This result establishes that the quenching groups are bound to the polymer chain.

Figure 5 illustrates the fluorescence decay of a MMA–2NMA copolymer film prior to conversion by photo-Fries products by 300-nm irradiation. Initially the decays of the unphotolyzed 2NMA copolymers are close to exponential, although improved fits are obtained with a sum of exponential terms:

$$I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \tag{7}$$

Table III lists the decay parameters of the four undegraded copolymer films. The deviations from exponentiality are slight and may merely reflect a distribution of chromophore environments in the film. They do not appear to arise from a small degree of photoreaction occurring in the film during the lifetime measurement itself, because decay curves recorded to different intensities in the maximum channel gave the same fitting parameters to within experimental error.

Table III
Results of Analysis of Fluorescence Decays of 1NMA and 2NMA Copolymers as Single and Double Exponentials

| sample | $\tau_f$, ns | $\chi_R^2$ | $A_1/A_2$[a,b] | $\tau_1$,[a,c] ns | $\tau_2$,[a,c] ns | $\chi_R^2$ |
|---|---|---|---|---|---|---|
| 1 | | | 0.65 | 4.8 | 13.5 | 1.56 |
| 2 | | | 1.00 | 7.2 | 17.9 | 1.11 |
| 3 | 17.1 | 2.50 | 0.23 | 6.6 | 18.5 | 1.45 |
| 4 | 22.4 | 1.55 | 0.29 | 15.0 | 24.0 | 1.12 |

[a] Decay curves analyzed according to eq 7. [b] Standard deviation in $A_1/A_2$ for any given decay curve is 2%; the estimated reproducibility for different experiments on the same sample is ±10%. [c] Standard deviations in $\tau_1$ and $\tau_2$ for any given decay curve are <0.1 ns; the estimated reproducibility for different experiments on the same sample is ±0.8 ns.

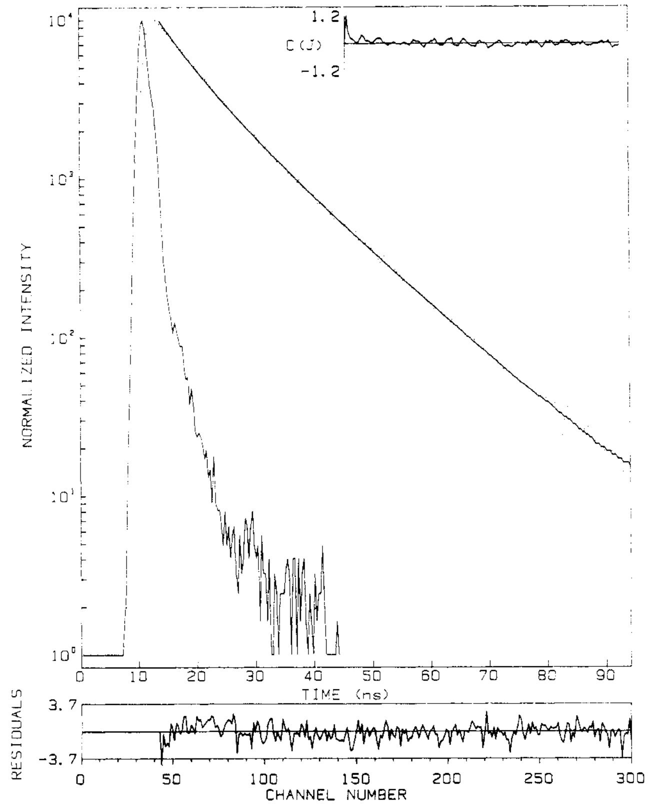

**Figure 6.** Fluorescence decay of the poly(MMA–2NMA) film of Figure 5 after 37 min of 300-nm irradiation in air. The smooth curve through the decay data points is the best-fit analysis using the model of ref 26, with donor and trap concentrations listed in Table VI. $\chi_R^2 = 1.37$.

Figures 6 and 7 show that conversion of copolymerized NMA to photo-Fries products is accompanied by a shortening of the $1/e$ decay time of the fluorophore and by increased deviation from exponentiality. For randomly distributed donors and acceptors, Förster's theory of long-range electronic excitation transfer predicts that the donor fluorescence decays should be described by

$$I_f(t) = B_1 \exp(-t/\tau_f) \exp[-2C/C_0(t/\tau_f)^{1/2}] \tag{8}$$

where $C$ is the acceptor concentration and the scaling factor $C_0$ is related to the Förster radius $R_0$ by

$$C_0 = 3000/2\pi^{3/2}N_AR_0^3 \tag{9}$$

In eq 9 $N_A$ is Avogadro's number and $R_0$ and $C_0$ are in units of cm and mol L$^{-1}$, respectively. Deviations from eq 8 are known to occur at high donor concentration and arise from

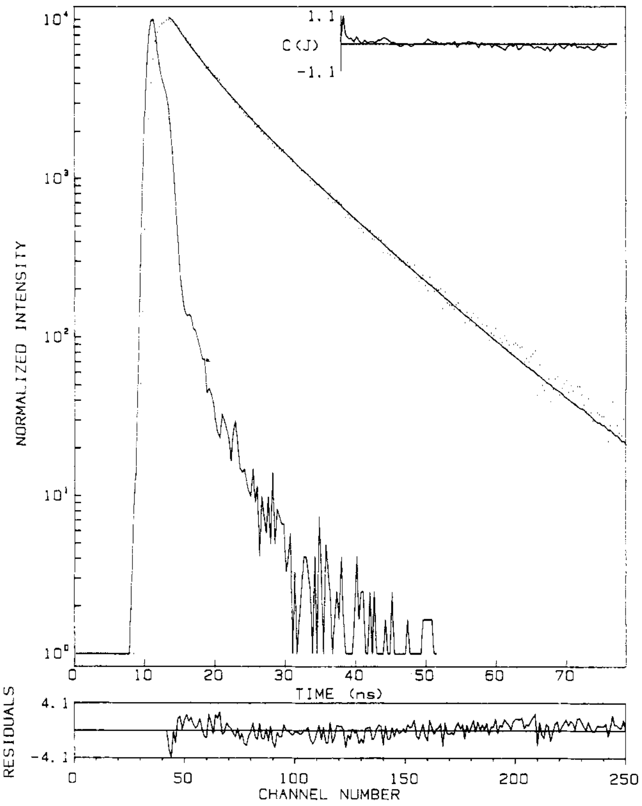

**Figure 7.** Fluorescence decay of the poly(MMA-2NMA) film of Figure 5 after 59 min of 300-nm irradiation in air. The smooth curve through the decay data points is the best-fit analysis using the model of ref 26, with donor and trap concentrations listed in Table VI. $\chi_R^2 = 1.54$.

**Table IV**
**Variation of Fitting Parameters $A_2$ and $A_3$ with Time of Irradiation of a Poly(MMA-*co*-2NMA) Film**[a]

| irrad time, min | $A_2$,[b] ns | $A_3$[c] | $\chi_R^2$ |
|---|---|---|---|
| 14 | 77.2 | 0.336 | 1.95 |
| 22 | 76.0 | 0.463 | 1.97 |
| 37 | 84.2 | 0.691 | 1.45 |
| 59 | 60.6 | 0.825 | 2.77 |

[a] Fluorescence decays at 337 nm fitted to eq 3 with $\tau_f$ fixed at 22.4 ns. [b] ±0.2. [c] ±0.002.

electronic energy migration between donors, a process which enhances the quenching efficiency and further shortens the donor fluorescence decay time.

We were unable to obtain meaningful fits of eq 8 to the experimental decays of the irradiated NMA copolymer films. In all cases the reduced $\chi^2$ values were greater than 5, with obvious systematic deviations between experimental and best-fit decays. To demonstrate that such deviations were significant, the same decay curves were analyzed with eq 3, which introduces an additional fitting parameter. Table IV summarizes the results of this analysis. The marked improvement in the $\chi_R^2$ values obtained with eq 3 suggests that the deviations from Förster decay kinetics are genuine. The term $A_2$ in eq 3 cannot simply be regarded as a relaxation of the restriction that $\tau_f$ be a constant from sample to sample, because the lifetime in the term $\exp[-2A_3(t/\tau_f)^{1/2}]$ remains unmodified. Two effects may contribute to the deviation from Förster kinetics: donor–donor transfer and deviations from a random chromophore distribution.

Electronic energy migration between donor chromophores leads to depolarization of the donor fluorescence.[33-37] Table V lists values of the fluorescence polarization $P$ of the NMA chromophore in copolymer films.

**Table V**
**Polarization $P$ of Fluorescence of Copolymerized 1NMA and 2NMA and of Model Compounds in Thin Films**

| sample | $\lambda_{ex}$, nm | $\lambda_{em}$, nm | $P$ |
|---|---|---|---|
| 1 | 300 | 340 | 0.19 |
| 2 | 300 | 340 | 0.18 |
| 3 | 290 | 330 | 0.19 |
| 4 | 290 | 330 | 0.14 |
| 2-naphthyl acetate | 300 | 326 | 0.22 |
| 2-naphthyl pivalate | 300 | 336 | 0.19 |

**Table VI**
**Best-Fit Donor and Trap Concentrations $C_D$ and $C_T$ in the Analysis of Fluorescence Decays of Irradiated Poly(MMA-*co*-2NMA) Films by the Method of Ref 26**

| irrad time, min | $C_D$,[a] M | $C_T$,[b] M | $\chi_R^2$ |
|---|---|---|---|
| 14 | 0.300 | $0.017_4$ | 1.37 |
| 22 | 0.239 | $0.021_8$ | 1.50 |
| 37 | 0.232 | $0.027_3$ | 1.37 |
| 59 | 0.200 | $0.034_6$ | 1.54 |

[a] ±2%. [b] ±1%.

These values of $P$ are nearly as large as those obtained for model compounds at concentrations of $10^{-4}$ M in polystyrene films and indicate the absence of extensive energy migration in these copolymers. Such a conclusion in no way contradicts earlier research on energy migration in naphthalene-containing homopolymers,[38] because in the copolymer films the naphthalene concentration is much lower, being approximately the same magnitude as the Förster concentration of 0.35 M (Table II) for excitation transfer between naphthalene chromophores.

Many different models have been developed in the literature to predict the effects of energy migration on fluorescence decay.[26,39-52] From these the Loring, Andersen, and Fayer model[26] was chosen for comparison with our experimental data for two reasons: it was derived explicitly for random distributions of donors and traps, and it does not make the simplifying assumption that energy migration is a diffusive process. This model predicts the time evolution of the donor fluorescence decay, given by eq 5. While the donor trapping function $G^D(t)$ is not analytical, an expression for its Laplace transform $G^D(s)$ was derived:

$$G^D(s) = \frac{[\hat{G}(s)]^2}{\hat{G}(s) - \tilde{\Delta}[0,\hat{G}(s)]} \tag{10}$$

The terms $\hat{G}(s)$ and $\tilde{\Delta}[0,\hat{G}(s)]$ are functions of $C_D$ and $C_T$, the reduced donor and acceptor concentrations, and of $\tau_f$, the donor decay time in the absence of quenchers. In addition the relative contributions of energy migration and Förster transfer are fixed by two terms $\alpha$ and $\beta$, which are functions of the relative values of $R_0$ for donor–donor and donor–trap transfer.

It was not possible to determine $C_D$ and $C_T$ precisely from the absorption spectra of the irradiated copolymer films, both because of spectral overlap and because two isomeric photo-Fries quenchers are generated during the photoreaction. Instead, $C_D$ and $C_T$ were allowed to vary slightly around the values determined spectroscopically. From selected values of $C_D$ and $C_T$, the fixed value of $\tau_f$ from Table III, and the fixed values of $R_0$ from Table II, donor fluorescence decays were calculated as described in the Experimental Section. Typical calculated donor decays are compared with the experimental decays in Figures 6 and 7. The agreement between experimental and calculated fluorescence decays is remarkable: only in the first 1–2 ns is there any systematic deviation. Table VI lists values of donor and acceptor concentrations determined

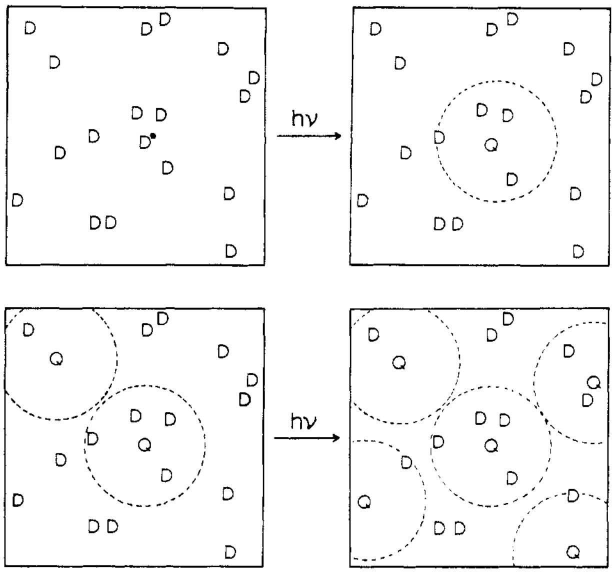

**Figure 8.** Conceptual illustration of the generation of a nonrandom distribution of quenching chromophores by a gradual photoreaction in a solid polymer film. Each new quencher Q deactivates photoexcited donors lying within the Förster radius for quenching, so that the formation of overlapping quenching domains is reduced.

for a copolymer film irradiated for different times. The concentrations listed in Table VI confirm that the efficient quenching of the naphthyl fluorescence occurs once the trap concentration has increased to 0.03 M, the critical concentration for Förster transfer to the photo-Fries products.

One feature of the analysis summarized in Table VI is of some concern: the reduction in the donor concentration during the photoreaction is not balanced by a corresponding increase in the quencher concentration. Admittedly, since the donor concentrations are low in these copolymer films, the effects of donor–donor excitation transfer are small, so that substantial changes in donor concentration have only a minor effect on the shape of the donor decay curves. It may be that there is a competing photoreaction which consumes copolymerized 2NMA without generating strongly absorbing products. An alternative explanation is suggested by the way in which the acceptor chromophores are generated in the films: the distribution of quenching sites in an irradiated film may not be exactly the random distribution assumed in Förster kinetics and in the model of ref 26. Figure 8 illustrates how the photo-Fries reaction in a solid polymer could generate a nonrandom product distribution. Once an acylnaphthol chromophore has been created at a particular site in the film, it effectively quenches all photoexcited donors within a 2.5-nm radius, so that the probability of generating a second acceptor near the first is reduced. On average only those NMA chromophores which are greater than 2.5 nm from an acceptor will react to generate additional quenching sites. The result is a slightly more uniform distribution of quenchers than could be obtained, for example, by mixing small-molecule photostabilizers into a solid polymer or by evaporating a solution of a polymer containing a copolymerized stabilizer. This tendency of the photo-Fries reaction to generate stabilizing groups separated by a distance on the order of $R_0$ creates a more uniform donor ensemble and diminishes the nonexponentiality of the donor fluorescence decays.

## Conclusions

The stabilizing effect of acylnaphthols obtained by the photo-Fries reaction in NMA copolymers is considerably greater than the low absorbance of these chromophores would predict. By observation of the effects of the photoreaction on the fluorescence of the unreacted NMA units, it was established unambiguously that the photoproducts exert their stabilizing effect by long-range electronic excitation transfer. This mechanism of polymer photostabilization has often been assumed but has proven difficult to verify conclusively. The generation of a more uniform concentration of photostabilizer by a photochemical reaction is an intriguing possibility, because it may result in a higher level of protection than could be achieved by dispersing the same concentration of a small-molecule stabilizer in the polymer.

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**Registry No.** 1NMA, 19102-44-4; 2NMA, 10475-46-4; (2NMA)·(styrene) (copolymer), 53640-72-5; (NMA)·(2NMA) (copolymer), 73970-14-6; (1NMA)·(styrene) (copolymer), 30175-66-7; (MMA)·(1NMA) (copolymer), 38783-77-6; 2-naphthol, 135-19-3; methacryloyl chloride, 920-46-7; 2-naphthyl acetate, 1523-11-1; 2-naphthyl pivalate, 1503-86-2.

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# Structure-Dependent Enthalpy Relaxation at the Glass Transition of Polystyrenes[†]

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ABSTRACT: Parameters of Moynihan's model for enthalpy relaxation at the glass transition of polystyrene are shown to be sensitive to polymer weight, molecular weight distribution, and filler content, and a tentative structural explanation for the observed changes is proposed.

## Introduction

According to a huge body of experimental evidence (e.g., ref 1–3), transition of a liquid substance into the glassy state (or vice versa) generally occurs over a more or less broad temperature interval, $\Delta T$, and is accompanied by a characteristic change of principal thermodynamic variables (specific heat $C$, thermal expansion coefficient $\alpha$, compressibility $\beta$, etc.). In most equilibrium theories of the glass transition it is implicitly assumed that $\Delta T = 0$, i.e., that change of the cited variables occurs in a jumplike fashion at a definite temperature $T_g$, which can thus be regarded as a "material constant" of a given substance.[4–6] On the other hand, kinetic theories concentrate on the analysis of the pattern of evolution of $C$, $\alpha$, and $\beta$ in the interval $\Delta T \neq 0$ as a function of thermal and mechanical prehistory.[7–11]

The theoretical basis of most current kinetic approaches is the assumption that during cooling at a constant rate, $q = \mathrm{d}T/\mathrm{d}t$, of the equilibrium liquid (i.e., melt) from a high temperature, $T_1 \gg T_g$, a moment is achieved when the rate of the structural rearrangements in the melt, which depends on thermal mobility of the molecules (or chain segments), starts to lag behind $q$. For this reason subsequent cooling of the sample will be accompanied by progressive deviation of its "instant" structure from the equilibrium one. Stated otherwise, at sufficiently low temperature, $T_2 < T_g$, a glassy substance will possess a "frozen-in" structure (or a set of structures) that the equilibrium melt would have at some "fictive" temperature, $T_2 < T_f \approx T_g$.

As shown by Moynihan,[13,14] temperature dependence of the structural parameter $T_f$ may be described by

$$T_f(T) = T_1 + \int_{T_1}^{T} \left\{1 - \exp\left[-\left(\int_{T'}^{T} \mathrm{d}T''/q\tau\right)^{\beta}\right]\right\} \mathrm{d}T' \qquad (1)$$

where $\tau = A \exp[X\Delta h/RT + (1 - X)\Delta h/RT_f]$ is the relaxation time, $\Delta h$ is the corresponding activation energy, $0 < X < 1$ is the nonlinearity parameter ($X = 1$ in the linear case), $0 < \beta < 1$ is the phenomenological measure of the width of the relaxation time spectrum ($\beta = 1$ for a single relaxation time), $R$ is the gas constant, and $A$ is a fitting constant.

Parameters entering eq 1 may be obtained by appropriate treatment of experimental observation of the evolution of a selected macroscopic property of a substance in the course of its cooling and heating. Having chosen relative enthalpy $\Delta H$ as a phenomenological characteristic of the structural state of a substance, one may calculate $T_f$, for example, at $T_2$ from the expression[13,14]

$$\Delta H(T_2) = \Delta H(T_f) - \int_{T_2}^{T_f} (\mathrm{d}\Delta H/\mathrm{d}T)_g \, \mathrm{d}T$$

which on account of a standard definition of specific heat, $C = \mathrm{d}\Delta H/\mathrm{d}T$, may be rewritten as

$$\int_{T_1}^{T_f} (C_1 - C_g) \, \mathrm{d}T' = \int_{T_1}^{T_2} (C - C_g) \, \mathrm{d}T'$$

Differentiation of the latter equation yields the following expression for the temperature coefficient of $T_f$:[13,14]

$$\frac{\mathrm{d}T_f}{\mathrm{d}T} = \frac{(C - C_g)|_T}{(C_1 - C_g)|_{T_f}} \qquad (2)$$

where $C$ is the relaxation part of specific heat in the glass transition interval. Thus, one has to search for optimum values of parameters from eq 1 that would provide minimum deviation of the calculated curves of "reduced" (i.e., nondimensional) specific heat obtained by differentiation of eq 1 from corresponding experimental curves at the same cooling rate constructed from eq 2.

Recently, Hodge et al.[15,16] made an attempt to find correlations between the parameters $\Delta h/R$, $X$, and $\beta$ and the molecular characteristics of a polymer. As will be shown below, numerical values of these parameters are also sensitive to structural changes of the same polymer pre-

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[†] Dedicated to Professor Dr. Josef Schurz on the occasion of his 60th birthday.

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