1138 *Macromolecules* 1980, *13*, 1138–1143

Photophysics and Photochemistry of Naphthyl Ester Polymers in Solution

L. Merle-Aubry,[1] D. A. Holden, Y. Merle,[1] and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.

Received February 13, 1980

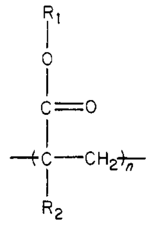
ABSTRACT: Homopolymers of 1- and 2-naphthyl acrylate and methacrylate have been synthesized, and their photochemistry and fluorescence behavior have been studied in THF at 25 °C. All four polymers undergo a photo-Fries reaction which leads to the introduction of quenching groups on the polymer chain. The polymers also exhibit intramolecular excimer fluorescence, with the ratio of excimer to monomer emission greater in the more flexible polyacrylates. Quantum yields of photochemical reaction are of the same magnitude as those of fluorescence. Irradiation of methacrylate homopolymers or copolymers with vinyl ketone monomers leads to random chain scission with low quantum yield, a process which enables determination of the Mark–Houwink viscosity laws for each polymer. The polyacrylates undergo cross-linking in competition with chain scission. Variations between the monomer fluorescence decay functions of the four polymers are attributed to differences in the nature of the chromophores and, to a lesser degree, to differences in chain flexibility.

The action of light on polymers whose repeating units contain the naphthalene chromophore continues to be studied from a number of viewpoints. Several authors have shown that copolymerized naphthalene-containing monomers may trap ultraviolet radiation, partially or completely suppressing the photoreactions of other chromophores on the polymer.[2,3] Naphthalene-containing polymers may exhibit intramolecular excimer fluorescence, and study of the phenomenon provides information on polymer structure and mobility, both in solution[4-7] and in the solid phase.[8,9] In a polymer containing a high density of aromatic chromophores around the main chain, energy transfer is possible. Because of its relevance to polymer photostabilization and its analogy to natural photosynthetic processes, energy transfer in naphthalene polymers, both in the singlet[10-12] and triplet[13,14] manifolds, is a field of considerable activity.

The detailed interpretation of photophysical results requires knowledge of basic properties of the polymer, such as tacticity, chain dimensions, chain flexibility, and whether the polymer undergoes simultaneous photochemical reaction on irradiation. Unfortunately, little of this information is available in the literature. Amerik et al. have photolyzed poly(1-naphthyl methacrylate) (P1NMA) and its copolymers with methyl methacrylate (MMA).[15] Quantum yields of chain scission were found to be considerably lower in P1NMA than in a copolymer containing predominantly MMA, a result attributed to excimer formation in the homopolymer. More detailed experiments are required, however, to understand this competition between photochemical and photophysical deactivation pathways.

Recently Keyanpour-Rad et al. described the effects of polymer structure on the fluorescence of polymers containing the carbazole chromophore.[16] This work represented an extension of earlier work by Johnson.[17] The extent of excimer fluorescence was shown to be particularly sensitive to the mode of attachment of the carbazole group to the polymer chain. Thus only one of the five polymers synthesized showed excimer emission at room temperature.

This paper represents a continuation of the investigation of the dependence of excimer photophysics on polymer structure, working with the simpler naphthalene chromophore. The four polymeric esters of naphthol were P1NMA, poly(2-naphthyl methacrylate) (P2NMA), poly(1-naphthyl acrylate) (P1NA), and poly(2-naphthyl acrylate) (P2NA). Since these polymers undergo photochemical as well as photophysical processes, they are unsuitable candidates for energy-transfer antennas. On the other hand, because the photolysis products have high extinction coefficients throughout the near-ultraviolet region, the irradiation of copolymerized naphthyl esters constitutes a potentially useful method for in situ generation of photostabilizers.



P1NMA, R_1 = α-naphthyl; R_2 = Me
P2NMA, R_1 = β-naphthyl; R_2 = Me
P1NA, R_1 = α-naphthyl; R_2 = H
P2NA, R_1 = β-naphthyl; R_2 = H

Experimental Section

Polymer Synthesis and Characterization. Acryloyl, methacryloyl, isobutyroyl, and pivaloyl chlorides were prepared from the corresponding acids and $SOCl_2$ and were fractionally distilled in vacuo immediately before use.[18] Commercial α- and β-naphthols were twice precipitated from aqueous NaOH solution by addition of HCl. They were then recrystallized from 4:1 H_2O–EtOH or chromatographed on alumina, eluting with ethanol. Monomers were prepared by the Schotten–Baumann condensation of freshly purified naphthol with acid chloride[11] and were purified by chromatography on alumina, eluting with benzene. Phenyl vinyl ketone (PVK) and phenyl isopropenyl ketone (PIPK) were prepared by literature methods.[19,20] These monomers and methyl vinyl ketone (MVK) were fractionally distilled from CaH_2 at reduced pressure before use. Polymers and copolymers were prepared by azobis(isobutyronitrile)-initiated free radical polymerization in degassed dry toluene at 60 °C. After three precipitations from chloroform into methanol and extraction with methanol in a Soxhlet apparatus, the polymers were dried and stored in the dark. Properties of the polymer samples are summarized in Table I. Molecular weights were determined by membrane osmometry in THF. The ketone contents of the copolymers were measured by IR spectroscopy on a Perkin-Elmer Model 625 instrument, using calibration curves obtained for the ketone bands of homopolymers of PVK, PIPK, and MVK. Molecular weight distributions were estimated by gel permeation chromatography on a Waters Model ALC/GPC 244 instrument, using THF as solvent.

Synthesis of Model Compounds. 1-Naphthyl pivalate was prepared from sodium α-naphthoxide and pivaloyl chloride by following the procedure for 1-NMA. The crude ester was purified by column chromatography on alumina, eluting with cyclohexane, and formed colorless needles (pentane): mp 34.5–35.0 °C (uncorrected); NMR ($CDCl_3$) δ 1.4 (s, 9 H, 3 CH_3), 7.1–8.0 (m, 7 H, Ar H); UV (Cary 14, THF) λ_{max} 317 (ε 224 M^{-1} cm^{-1}), 313 (392), 291 (4500), 281 (6340), 272 (5560) nm. 1-Naphthyl isobutyrate

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Table I
Properties of the Naphthyl Ester Polymer Samples

polymer	% ketone in feed	% ketone in polymer	% convrsn	[η],[a] dL g^{-1}	$10^{-4}\overline{M}_n$	γ_0[b]
P1NMA	0	0	55		5.1	
P1NMA-MVK	5	<5	47	0.49	15.9	2.8
P1NMA-PVK	4	3.2	56		7.8	2.3
P1NMA-PIPK	6	4.0	35			
P2NMA	0	0	67		8.6	4
P2NMA-MVK	5	<5	41	0.81	34.4	2.9
P2NMA-PIPK	6	4.4	40		12.8	2.2
P1NA	0	0	43	0.49	8.6	
P2NA	0	0	60	0.57	9.7	
P2NA-MVK	4	<4	65	0.31	5.7	

[a] In THF, 25 °C. [b] Polydispersity, as estimated from GPC curve.

(mp 28-30 °C), 2-naphthyl pivalate (mp 65.5-66.0 °C), and 2-naphthyl isobutyrate (mp 42.5-43.0 °C) were obtained similarly.

2-Aceto-1-naphthol was prepared by the Friedel-Crafts acylation of 1-naphthol in acetic acid[21] and was purified by several recrystallizations from ethanol: mp 95-96 °C; UV (THF) λ_{max} 364 (ϵ 5400), 306 (2240), 294 (5350), 284 (5580) nm.

4-Aceto-1-naphthol was prepared by the Friedel-Crafts acylation of 1-naphthol in nitrobenzene at 0 °C[22] and was purified by several recrystallizations from 80% ethanol, followed by vacuum sublimation at 140 °C: mp 196.5-197 °C; UV (THF) λ_{max} 324 (ϵ 10 200) nm.

1-Aceto-2-naphthol was obtained by the $AlCl_3$-catalyzed Fries reaction of 2-naphthyl acetate[23] and was purified by fractional distillation at high vacuum, followed by two recrystallizations from ACS hexanes: mp 61-63 °C; UV (THF) λ_{max} 360 (ϵ 3140), 337 (3590), 309 (4930) nm.

6-Aceto-2-naphthol was prepared by the Friedel-Crafts acylation of 2-methoxynaphthalene in nitrobenzene at 0 °C.[24] The purified ether was demethylated with $AlCl_3$ in refluxing xylene,[25] recrystallized from benzene, and sublimed in vacuo at 160 °C: mp 171-172 °C; UV (THF) λ_{max} 332 sh (ϵ 5170), 312 (11 900) nm.

Photolysis Studies. Polymers and their model compounds in THF at 25 °C were irradiated under nitrogen in 1-cm quartz cells. THF was refluxed over $LiAlH_4$ for 16 h and fractionally distilled under nitrogen. For studies of the photo-Fries reaction a Bausch & Lomb high-pressure Hg lamp and grating monochromator provided 280-nm radiation. Changes in the UV spectra of the irradiated solutions were recorded on a Cary 14 UV spectrometer. The absolute incident light intensity at 280 nm was monitored by potassium ferrioxalate actinometry[26] and was on the order of 3×10^{-10} einstein s^{-1}. The slopes of plots of absorbance change vs. irradiation time were measured at two wavelengths: 324 and 365 nm for the esters of 1-naphthol and 332 and 360 nm for the 2-naphthyl esters. From the rates of absorbance change at these two wavelengths quantum yields of product formation were calculated, using the extinction coefficients of the model acetonaphthols to approximate those of the polymeric acylnaphthols. Allowance was made for the partial overlap of the absorption bands of the isomeric photoproducts.[27]

The parameters of the Mark-Houwink viscosity equation for the naphthyl ester polymers were determined by automatic viscometry,[28] following the method of Kilp and Guillet.[29] Solutions were irradiated through a 313-nm interference filter with light from a 250-W medium-pressure Hg lamp (CGE). Intrinsic viscosities were determined by the single-point method outlined previously.[29]

Fluorescence Studies. Fluorescence spectra of deoxygenated THF solutions were recorded on a Hitachi Perkin-Elmer MPF 2A spectrofluorimeter and were corrected for the wavelength dependence of the detector response.[10] Quantum yields were measured by the method described previously,[11] using carefully purified α-naphthol as the standard.[10]

Polymer fluorescence decays were measured by single-photon counting as described in previous publications.[10,11] The 10^{-4} M THF solutions were degassed to a residual pressure of 5×10^{-4} mmHg. Samples were excited at 280 nm and fluorescence was detected at 325 nm through the combination of a monochromator and a Corning 7-51 filter (310-410 nm band-pass). All samples were prepared in dim light and were used for only one single-photon-counting or steady-state fluorescence experiment, in order to prevent interference from quenching by photodegradation products.

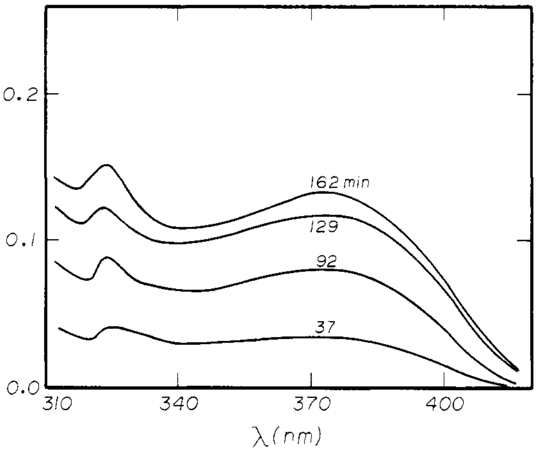


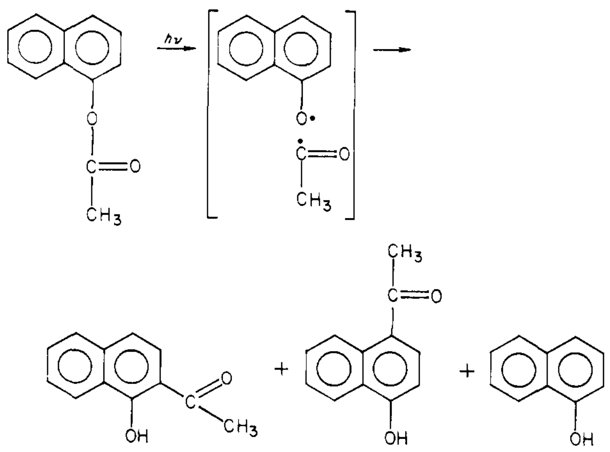
Figure 1. Absorbance change ΔA on 280-nm irradiation of P1NMA in deoxygenated THF at 25 °C.

Results and Discussion

Photo-Fries Reaction. Figure 1 illustrates the absorbance changes which accompany the 280-nm irradiation of an oxygen-free THF solution of P1NMA. Overlapping bands at 370 and 325 nm (partly hidden beneath the absorption band of the polymer) are clearly visible. Quantum yields of absorbance change are linear with irradiation time up to the point where competing absorption by the photolysis products begins to occur. On the strength of the close correspondence of these new absorption bands with those of model compound acetonaphthols, it is proposed that the naphthyl ester polymers undergo degradation by a photo-Fries reaction.

The photoreaction of the analogous model compound was studied by Stratenus, who showed that the photo-Fries reaction occurred in 1- and 2-naphthyl acetates.[30,31] A mixture of acylnaphthols results; escape of the naphthoxy radical from the solvent cage leads to the formation of minor amounts of 1- and 2-naphthols, as illustrated in reactions 1 and 2.[31,32]

Table II lists quantum yields of fluorescence and of acylnaphthol formation for the four naphthyl ester polymers and their model compounds. It was not possible to analyze for free naphthol by UV spectrophotometry; however, earlier work suggested that the quantum yields of naphthol formation may be relatively insignificant.[31] The data of Table II point to several conclusions. Fluorescence quantum yields ϕ_f are higher for 2-naphthyl esters than for 1-naphthyl esters, resulting in part from the greater photochemical reactivity of the 1-naphthyl



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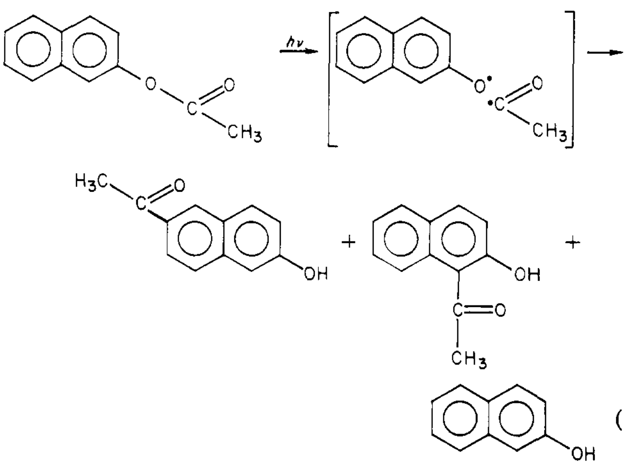

(2)

compounds. Photo-Fries product quantum yields are in all cases significant in comparison with ϕ_f. Finally, quantum yields of acylnaphthol formation are not much lower in the polymer than in the corresponding model compound. Similar results were obtained by Li and Guillet for the photo-Fries reaction of poly(phenyl acrylate).[33] These authors concluded from the relative insensitivity of product quantum yields to environment that this photoreaction proceeded with only a small amount of molecular motion.

The polymer-bound hydroxynaphthones are potential UV-screening agents since they have high extinction coefficients in the near-UV region and because the absorbed light is dissipated nonphotochemically. In this way they resemble *o*-hydroxybenzophenones,[34] with the added advantage that both isomers are active.

Fluorescence Measurements. Figure 2 shows the steady-state fluorescence spectra of the four naphthyl ester polymers in deoxygenated THF at 28 °C. All of the polymers exhibit intramolecular excimer emission in addition to the "monomer" emission of the unassociated naphthalene chromophore, with the polyacrylates exhibiting larger contributions from excimer fluorescence. This result is significant because it is known from a variety of techniques, including T_g measurements[35] and fluorescence polarization studies,[36] that the rate of rotation about the main chain is greater in polyacrylates than in the corresponding polymethacrylates.

The fluorescence decay functions of the free naphthalene chromophore were found to be nonexponential, as observed for several other naphthalene-containing polymers.[4,5,10] Iterative reconvolution of a decay law of the form shown in eq 3 gave adequate fits to these monomer decay curves.

$$I_M(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (3)$$

Table II
Quantum Yields ϕ_f and ϕ of Fluorescence and of Photo-Fries Product Formation for Naphthyl Ester Polymers and Their Model Compounds[a]

compound	ϕ_f[b]	ϕ	ϕ
		4-acyl-1-naphthol[b]	2-acyl-1-naphthol[b]
P1NA	0.009	0.040	0.026
P1NMA	0.016	0.036	0.029
1-naphthyl isobutyrate	0.022	0.13	0.069
1-naphthyl pivalate	0.027	0.089	0.050
		6-acyl-2-naphthol	1-acyl-2-naphthol
P2NA	0.049	0.055	0.006
P2NMA	0.068	0.028	0.004
2-naphthyl isobutyrate	0.080	0.054	0.006
2-naphthyl pivalate	0.074	0.069	0.002

[a] λ_{ex} = 280 nm, in THF under N_2 at 25 °C. [b] Error ±20%.

Table III
Decay Parameters of Naphthalene-Containing Polymers in Degassed THF at 25 °C[a]

polymer	τ_1, ns	τ_2, ns	A_1/A_2	τ_{model}, ns
P1NA	1.4	9.0	6.8	11.8
P1NMA	1.9	7.9	7.7	10.2
P2NA	2.7	18.6	2.0	16.9
P2NMA	6.0	20.5	2.4	16.4

[a] λ_{ex} = 280 nm, λ_{em} = 325 nm, decay curves fitted to eq 3.

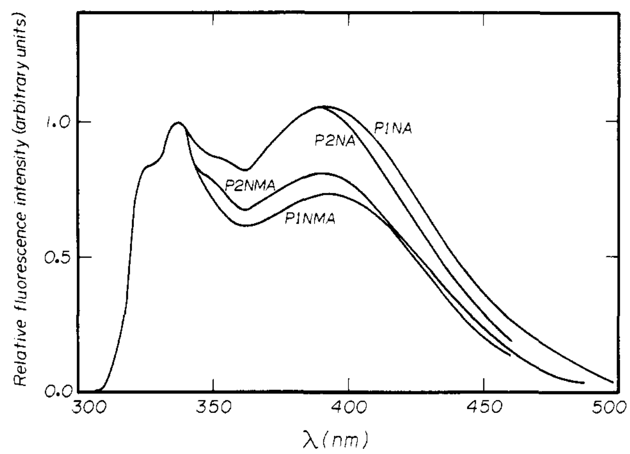

Figure 2. Corrected fluorescence spectra of 10^{-4} M naphthyl ester polymers in THF at 28 °C (λ_{ex} = 280 nm). Spectra are normalized to the same intensity at 337 nm.

Values of τ_1, τ_2, and A_1/A_2 for the four polymers are listed in Table III, together with fluorescence decay times of the corresponding model compounds. Values of the reduced sum of the squares of the residuals, χ_R^2, are between 1 and 3. The value of attempting to reduce χ_R^2 further by choosing a more complex fitting function is complicated by the problem of guessing the physical significance of such a function. As Table III shows, each monomer curve contains a rapidly decaying component and a minor component decaying with a lifetime similar to that of the model compound. Whether the slowly decaying component of monomer emission arises from excimer dissociation as in the well-known Birks kinetic scheme[37] or from unquenched isolated naphthalene units[38] cannot be decided without further experimental work.

Nevertheless, some trends are evident from the results of Table III. Lifetimes τ_1 and τ_2 are longer for the 2-

Table IV
Main Chain Scission Quantum Yields of Polymers in Solution[a]

polymer	ϕ_{cs}[b]
P1NMA	0.019
P1NMA-MVK	0.007
P1NMA-PVK	0.020
P1NMA-PIPK	0.012
P1NMA-PIPK	$<10^{-4}$ (366 nm)
P2NMA	0.002
P2NMA-MVK	0.002
P2NMA-PIPK	0.005
P2NMA-PIPK	0.0005 (366 nm)
PMMA-MVK	0.20[c] (ref 39)
PS-PVK	0.49[c] (ref 40)
PS-PIPK	0.26[d] (ref 41)

[a] In THF at 25 °C, irradiation under N_2 at 313 nm unless specified otherwise. [b] Error ± 20%. [c] In benzene. [d] In 1,2-dichloroethane.

naphthyl ester polymers than in the 1-naphthyl series. Model compound fluoresence decay times show that this is a property of the chromophores themselves and probably reflect in part the greater photochemical reactivity of the 1-naphthyl series. Secondly, values of the short lifetimes are lower for the polyacrylates than for the less flexible polymethacrylates. The trapping of electronic energy at an excimer site is seen to occur more rapidly in a flexible polymer than in one where rotation is more restricted. Ueno and Osa have also explored the relationship between chain stiffness and excimer formation.[12] These authors showed that energy migration could still occur in a polymer so rigid that excimer sites could not form. Our present understanding of these polymers suggests that an inflexible main chain suppresses excimer formation not by preventing energy transfer between chromophores but by preventing chromophores from encountering each other within the excited-state lifetime.

Studies of Main-Chain Scission. Recently, Kilp and Guillet have shown that random photochemical chain scission provides a facile route to polymers of constant polydispersity but having different molecular weights.[29] Simultaneous measurement of intrinsic viscosity $[\eta]$ and molecular weight M enables determination of the parameters K and a in the Mark-Houwink equation.

$$[\eta] = KM^a \tag{4}$$

Both P1NMA and P2NMA and their copolymers with vinyl ketone monomers undergo random chain scission on irradiation at 313 nm. Initial quantum yields ϕ_{cs} are low, as shown in Table IV. Chain scission in the homopolymers appears to be a property of the naphthyl ester linkage; thus ϕ_{cs} is below the limit of detection ($<10^{-4}$) in poly(2-vinylnaphthalene), for example. Copolymers of vinyl ketones with nonquenching monomers, such as styrene or methyl methacrylate, have ϕ_{cs} from 0.2 to 0.5.[39-41] By contrast, ϕ_{cs} is negligibly small in P1NMA-PVK and P2NMA-PIPK on direct excitation of the polymer ketone at 366 nm.

The results of these experiments can be best explained by consideration of the energy level diagram shown in Figure 3. It is seen that whereas the singlet state of naphthyl esters lies above that of the ketones, the triplet energy level of the naphthyl group is lower than that of the triplet of the aromatic ketone.[42] Thus one can expect energy transfer to occur from naphthalene singlets to ketone singlets and from the ketone triplet to the naphthalene triplet. In all of the polymers synthesized in this work, the naphthyl ester chromophore is in considerable excess and will absorb most of the light accepted by the polymer chain (except when irradiation is at 366 nm). Furthermore, it has been shown previously[10] that there is efficient singlet energy transfer along polymer chains from naphthalene to naphthalene. As shown by this work and also by Amerik et al.,[15] there is a chain-scission process in P1NMA with a quantum yield of approximately 0.02. The results of the present experiments can best be explained if one postulates that this value represents the approximate quantum yield of chain scission from the naphthyl ester singlet state and that the quantum yield of chain scission from the naphthyl ester triplet is low, possibly close to zero. This must be the case in order to explain the very low quantum yields for copolymers of 1- and 2-NMA with PIPK irradiated at 366 nm. Quantum yields were less than 10^{-4} and 0.0005, respectively. At this wavelength, only the PIPK chromophore would be absorbing light and the energy reaching the naphthalene ester chromophores would then be only triplet energy from energy transfer from the PIPK triplet. That this energy exchange process is highly efficient is shown by the fact that the quantum yield is at least 3 orders of magnitude smaller than would be expected from a styrene-PIPK copolymer where energy transfer from the isopropenyl ketone is not possible.

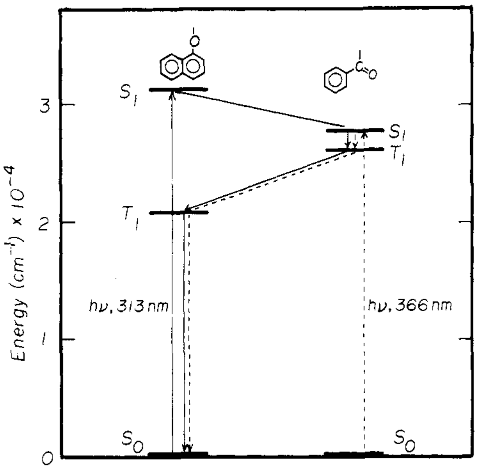

Figure 3. Energy level diagram for poly(1-NMA-PIPK). Also shown are the principal deactivation pathways on excitation of naphthalene at 313 nm (—) and on excitation of aromatic ketone at 366 nm (---).

Table V
Total Fluorescence Quantum Yields of NMA Homopolymers and Copolymers with Vinyl Ketone Monomers[a]

sample	ϕ_f[b]	sample	ϕ_f[b]
P1NMA	0.016	P2NMA	0.068
P1NMA-PVK	0.008	P2NMA-MVK	0.058
P1NMA-PIPK	0.012	P2NMA-PIPK	0.059

[a] In THF under N_2, λ_{ex} = 280 nm. [b] Precision ±10%, absolute error ±20%.

In all cases, the quantum yield of chain scission in vinyl ketone containing copolymers is several orders of magnitude less than in polymers such as polystyrene and methyl methacrylate which do not quench the triplet ketone. Therefore, one must conclude that at these low concentrations of ketone monomer, where naphthalene groups are adjacent to each carbonyl group, an efficient transfer of triplet energy occurs from the ketone to the naphthalene, resulting in a substantial reduction in quantum yield. The reduction in quantum yield of fluorescence from the naphthyl ester, shown in Table V, indicates that there is a measurable transfer of excitation energy from the naphthalene singlet to the ketone singlet. However, in the case of copolymerized aromatic ketones, this does not re-

Table VI
Mark–Houwink Parameters K and a and Steric Factors σ for P1NMA and P2NMA in THF at 25 °C

polymer	K, dL g^{-1}	a	σ	ref
P1NMA	1.21×10^{-3}	0.50	3.56	this work
P2NMA	3.06×10^{-4}	0.62	3.18	this work
P2NMA	0.907×10^{-4}	0.69	3.1	45
P2NMA[a]	1.47×10^{-4}	0.63	3.1–3.3	46

[a] In benzene.

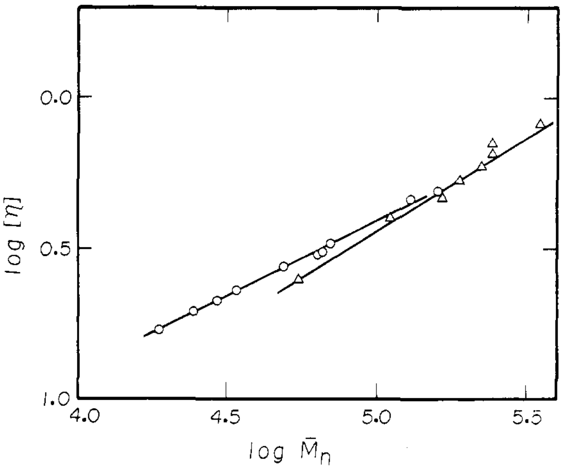

Figure 4. Variation of intrinsic viscosity [η] with molecular weight M in THF at 25 °C: (○) P1NMA-MVK; (△) P2NMA-MVK.

sult in the sensitized decomposition of the polymer because there is efficient transfer of triplet energy back to naphthalene. On the other hand, the methyl vinyl ketone copolymers may undergo slight sensitization by singlet energy transfer from naphthalene because the slower rate of intersystem crossing in these aliphatic ketones leads to measurable singlet-state photoreactivity.[43] Such photosensitization has been observed by Wagner[44] in studies of singlet energy transfer to aliphatic ketones in concentrated solutions of 1-methylnaphthalene.

The results for 2-naphthyl esters show that the quantum yield for chain scission is significantly lower than in the 1-naphthyl esters, being of the order of 0.002. Possibly there is a greater steric resistance in the 2-naphthyl ester to the formation of the cyclic six-membered transition state necessary for the type II scission to occur. These results are further confirmation of the fact that energy transfer is effective between donors and acceptors on adjacent units on polymer chains.

Solution Properties. Solution properties of the polymers may still be determined, even when the nature of the chain-breaking reaction is not known. The variation of [η] with M is illustrated for P1NMA and P2NMA in Figure 4. Table VI lists K and a values determined for the polymers by the method of Kilp and Guillet.[29] The P2NMA values agree fairly well with literature values:[45,46] the results of Hadjichristidis and Desreux[45] were determined on P2NMA samples of much higher molecular weight. Also listed in Table VI are values of the conformational factor σ, defined in eq 5.

$$\sigma = [\langle r^2\rangle_0/\langle r^2\rangle_{0f}]^{1/2} \tag{5}$$

In eq 5, $\langle r^2\rangle_0^{1/2}$ and $\langle r^2\rangle_{0f}^{1/2}$ are the root-mean-square end-to-end chain lengths of the real polymer in a Θ solvent and of a hypothetical freely rotating chain with tetrahedral bond angles. These in turn are calculated by eq 6–8,[47]

$$\langle r^2\rangle_{0f}^{1/2} = 0.308\bar{P}_n^{1/2} \quad \text{in Å} \tag{6}$$

$$K_\Theta = \Phi_\Theta[\langle r^2\rangle_0/M]^{3/2} \tag{7}$$

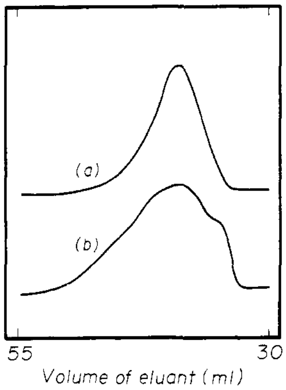

Figure 5. GPC traces of (a) initial and (b) photodegraded P2NA-MVK in THF.

where $\bar{P}_n$ is the number-average degree of polymerization, Φ_Θ is the universal viscosity constant for a random-coil polymer,[48] K_Θ is the value of the Mark–Houwink constant K in a Θ solvent, and M is taken to be the number-average molecular weight. K_Θ was determined for P2NMA from its viscosity–molecular weight relationship in THF, using the Stockmayer–Fixman equation[49]

$$[\eta]/M^{1/2} = K_\Theta + 0.51\Phi_\Theta BM^{1/2} \tag{8}$$

where the parameter B is a measure of polymer–solvent interactions. Values of σ of 3.6 and 3.2 were obtained for P1NMA and P2NMA, respectively. These are larger than those of poly(2-vinylnaphthalene) (3.1),[50] poly(N-vinylcarbazole) (2.8),[51] or polystyrene (2.2)[52] and suggest that the barrier to main-chain rotation is exceptionally large in poly(naphthyl methacrylates).

The irradiation of dilute solutions of P2NA or P1NA at 313 nm resulted in a large drop in [η] but only a moderate change in molecular weight. Calculated values of the exponent a ranged from 1.3 to 1.8, unreasonably large for what is undoubtedly a randomly coiled polymer. Figure 5 shows GPC curves of initial and irradiated P2NA-MVK samples. The curve of the irradiated sample is broadened and shows the presence of high molecular weight material. It appears that photochemical cross-linking occurs in the polyacrylates. The resulting continuous increase in polydispersity with irradiation time leads to spurious values of K and a.[53]

Angier et al. have shown that anomalously large values of a for polyisoprene resulted from cross-linking, leading to a change in polydispersity with mastication time.[54] Several authors have attributed a rapid drop in [η] on irradiation of poly(vinylbenzophenone) solutions to intramolecular cross-linking rather than chain scission.[55,56] Polyacrylates possess a tertiary hydrogen which renders them more susceptible to radical cross-linking than the corresponding polymethacrylates. Poly(methyl acrylate), for example, tends to cross-link when irradiated, whereas poly(methyl methacrylate) degrades by chain scission under the same conditions.[34]

In summary, photochemical processes occur with sufficiently high quantum yields in naphthyl ester polymers that they cannot be ignored in interpreting the photophysics of these polymers. There are differences in fluorescence quantum yields and decay times between 1-naphthyl ester polymers and 2-naphthyl ester polymers. Since similar contrasts are displayed by small-molecule model compounds, they are attributed to intrinsic differences in photochemical reactivity between the two chromophores. Additional lifetime and quantum yield variations between polyacrylates and polymethacrylates are attributed to the greater main-chain flexibility of the polyacrylate series.

References and Notes

(1) Permanent address: Université de Rouen, Faculté des Sciences et des Techniques, 76130 Mont-Saint-Aignan, France.
(2) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 1405 (1970).
(3) I. Lukac, P. Hrdlovic, Z. Manasek, and D. Bellus, *J. Polym. Sci., Part A-1*, **9**, 69 (1971).
(4) K. P. Ghiggino, R. D. Wright, and D. Phillips, *Chem. Phys. Lett.*, **53**, 552 (1978).
(5) J. S. Aspler and J. E. Guillet, *Macromolecules*, **12**, 1082 (1979).
(6) Y. Nishijima, Y. Sasaki, M. Tsujisaki, and M. Yamamoto, *Rep. Prog. Polym. Phys. Jpn.*, **15**, 453 (1972).
(7) Y.-C. Wang and H. Morawetz, *Makromol. Chem., Suppl.*, **1**, 283 (1975).
(8) C. W. Frank and M. A. Gashgari, *Macromolecules*, **12**, 163 (1979).
(9) R. F. Ried and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 231 (1978).
(10) D. A. Holden and J. E. Guillet, *Macromolecules*, **13**, 289 (1980).
(11) J. S. Aspler, C. E. Hoyle, and J. E. Guillet, *Macromolecules*, **11**, 925 (1978).
(12) A. Ueno and T. Osa, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 539 (1978).
(13) N. F. Pasch and S. E. Webber, *Macromolecules*, **11**, 727 (1978).
(14) R. B. Fox, T. R. Price, R. F. Cozzens, and W. H. Echols, *Macromolecules*, **7**, 937 (1974).
(15) Y. Amerik, Y. Y. Bairamov, and B. A. Krentsel, *Zh. Prikl. Spektrosk.*, **18**, 1023 (1973).
(16) M. Keyanpour-Rad, A. Ledwith, A. Hallam, A. M. North, M. Breton, C. Hoyle, and J. E. Guillet, *Macromolecules*, **11**, 1114 (1978).
(17) G. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
(18) S. Kasman and A. Taurins, *Can. J. Chem.*, **34**, 1261 (1956).
(19) E. Selegny, L. Merle-Aubry, and N. Thoai, *Bull. Soc. Chim. Fr.*, 3166 (1967).
(20) W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 649 (1946).
(21) O. N. Witt and O. Braun, *Ber. Dtsch. Chem. Ges.*, **47**, 3216 (1914).
(22) M. Akram and R. D. Desai, *Proc. Indian Acad. Sci., Sect. A*, **11**, 149 (1940).
(23) K. Fries, *Ber. Dtsch. Chem. Ges.*, **54**, 711 (1921).
(24) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 864 (1934).
(25) K. Fries and K. Schimmelschmidt, *Ber. Dtsch. Chem. Ges.*, **58**, 2835 (1925).
(26) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966.
(27) D. F. Boltz, "Selected Topics in Modern Instrumental Analysis", Prentice-Hall, New York, 1952, p 150.
(28) T. Kilp, B. Houvenaghel-Defoort, W. Panning, and J. E. Guillet, *Rev. Sci. Instrum.*, **47**, 1496 (1976).
(29) T. Kilp and J. E. Guillet, *Macromolecules*, **10**, 90 (1977).
(30) J. L. Stratenus, Ph.D. Thesis, Leiden, 1966.
(31) D. Bellus, *Adv. Photochem.*, **8**, 109 (1971).
(32) Y. Ohto, H. Shizuka, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **47**, 1209 (1974).
(33) S.-K. L. Li and J. E. Guillet, *Macromolecules*, **10**, 840 (1977).
(34) B. Ranby and J. F. Rabek, "Photodegradation, Photooxidation and Photostabilization of Polymers", Wiley, New York, 1975.
(35) M. C. Shen and A. Eisenberg, *Rubber Chem. Technol.*, **43**, 95 (1970).
(36) A. M. North and I. Soutar, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1101 (1972).
(37) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1971.
(38) D. A. Holden, P. Y.-K. Wang, and J. E. Guillet, *Macromolecules*, **13**, 295 (1980).
(39) Y. Amerik and J. E. Guillet, *Macromolecules*, **4**, 375 (1971).
(40) H. C. Ng and J. E. Guillet, *Macromolecules*, **11**, 937 (1978).
(41) K. Sugita, T. Kilp, and J. E. Guillet, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1901 (1976).
(42) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.
(43) E. Dan, A. C. Somersall, and J. E. Guillet, *Macromolecules*, **6**, 228 (1973).
(44) P. J. Wagner, *Mol. Photochem.*, **3**, 169 (1971).
(45) N. Hadjichristidis and V. Desreux, *J. Macromol. Sci., Chem.*, **6**, 1227 (1972).
(46) K. G. Berdnikova, G. V. Tarasova, V. S. Shaska, N. A. Nikitiu, and G. V. Dyuzhev, *Vysokomol. Soedin.*, **6**, 2057 (1964).
(47) J. Brandrup and E. H. Immergut, Eds., "Handbook of Polymer Science", Wiley, New York, 1966. See ref 51 for a typical application.
(48) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapter 14.
(49) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).
(50) V. E. Eskin and O. Z. Korotkina, *Vysokomol. Soedin.*, **2**, 272 (1960).
(51) G. Sitaramaiah and D. Jacobs, *Polymer*, **11**, 165 (1970).
(52) M. Kurata and W. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).
(53) T. L. Nemzek and J. E. Guillet, *Macromolecules*, **10**, 94 (1977).
(54) D. J. Angier, W. T. Chambers, and W. F. Watson, *J. Polym. Sci.*, **25**, 129 (1957).
(55) D. David, W. Demarteau, and G. Geuskens, *Polymer*, **10**, 21 (1969).
(56) G. Sanchez, Thesis, Université Louis-Pasteur de Strasbourg, 1975.

Laser Photolysis Studies of Excited-State Interactions of Poly(*N*-vinylcarbazole) and *N*-Isopropylcarbazole with Dimethyl Terephthalate

Uri Lachish, Robert W. Anderson, and David J. Williams*

Xerox Corporation, Webster Research Center, Webster, New York 14580.

Received December 26, 1979

ABSTRACT: The excited-state processes leading to exciplex formation and photoinduced electron transfer between excited poly(*N*-vinylcarbazole) (PVCz) and dimethyl terephthalate (DMT) and between its monomeric analogue *N*-isopropylcarbazole (NIPC) and DMT have been characterized by picosecond and nanosecond photolysis techniques. Comparison of absorption spectra of the transient species and their time evolution reveals the role of the specific polymeric environment on exciplex structure and dynamics. In toluene the absorption spectra in both the polymer and monomer systems indicate charge-transfer character in the exciplex state. However, the cation portion of the exciplex spectrum in the polymer is different from that in the monomer and indicates interaction of the carbazole cation with neighboring carbazole groups along the polymer chain. Exciplex decay in NIPC–DMT leads to enhancement of the NIPC triplet population while in the polymer system no triplet formation is observed. In dimethylformamide (DMF) dissociation to free ions is observed in both the polymer and monomer systems. Picosecond data indicate that molecular complexation is absent in PVCz–DMT prior to excitation and occurs by a diffusional process following excitation of the polymer.

The primary photophysical and photochemical processes in polymers have been the subject of intense interest in recent years. Structural features are often encountered in polymeric systems which alter the nature of excited-state

0024-9297/80/2213-1143$01.00/0