Singlet Energy Transfer in a 1-Naphthyl Methacrylate–9-Vinylanthracene Copolymer

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ABSTRACT: Studies have been made of electronic energy transfer from the naphthalene groups in poly(1-naphthyl methacrylate) to vinylanthracene traps located at chain ends. It is shown that the transfer is strictly intramolecular in dilute solution, and that the efficiency of transfer depends on the solvent power, being greater in solvents which tend to reduce the dimensions of the random coil. Studies of fluorescence decay times by photon counting suggest that the transfer of energy takes place in times of 1 ns or less, and temperature studies indicate that transfer occurs from naphthyl monomer rather than the excimer.

Excimer formation has been observed in many polymers bearing aromatic side groups (polystyrene, poly(vinylnaphthalene), etc.).[2-11] The distinguishing feature of polymer excimers in dilute solution (10^{-3} M in monomer groups) is that they are completely intramolecular and thus they are independent of concentration.

The excimer intensity in polymers (expressed as the excimer to monomer ratio, I_e/I_m) does not depend on the viscosity of the pure solvent. It does, for most polymers, depend on whether the solvent is "good" (chain expanding) or "poor" (chain contracting). For example, in poly(1-naphthyl methacrylate) (PNMA)[3] and in polystyrene,[4] excimer formation is greatest in poor polymer solvents and least in good polymer solvents. This is usually explained in terms of chain contraction in the poor solvent, resulting in a smaller interchromophore distance.

There exist many cases in which excimer formation is but one of several processes for the deactivation of singlet energy. Another example of singlet energy transfer involves two unlike chromophores in the same molecule. Early systems of this type are the 9-anthracenylnaphthylalkanes (n = 1,2,3).[12] Only anthracene emission was seen when the naphthyl group was excited at 280 nm. Similar effects are well known in biological systems, where long-range Förster transfer can act as a "spectroscopic ruler" for molecular dimensions and structure.

The mechanism of emission of excitation energy received by a trap in a polymer chain may be analogous to several well-known cases of "doped" crystals. An anthracene crystal with a small amount of added tetracene[13] shows complete quenching of the expected anthracene emission when excited in the UV. Tetracene emission only is seen. In the case of this crystal system, the energy transfer process arises from a long-range exciton transfer with termination at the tetracene traps.

Fox and co-workers have studied the energy transfer process of polystyrene copolymerized with (ca. 1%) 1-vinylnaphthalene. They found that the predominance of the styrene excimer traps did not prevent transfer to the few naphthalene traps.[8]

In the present work, the process of energy transfer to trap sites in a high molecular weight polymer was studied by observing the effect of solvent and temperature on the photoemission characteristics of a poly(1-naphthyl methacrylate)–9-vinylanthracene copolymer (PNMA–VA).

Experimental Section

Methacrylyl chloride (Pfalz & Bauer) was distilled before use. Isobutyryl chloride was prepared from isobutyric acid and thionyl chloride according to the method of Kasman and Taurins.[14] 1-Naphthyl methacrylate monomer (NMA) was prepared by a standard Schotten–Baumann reaction between sodium 1-naphtholate and the corresponding acid chloride.[15] The esters were extracted with ether, washed with dilute NaOH and water, dried, and vacuum distilled. NMA monomer was distilled from a small amount of copper powder (which acts as an inhibitor to polymerization) and recrystallized from pentane at room temperature (NMA: mp 39–41 °C, bp 125 °C (1 Torr); NIBA: mp 28–31 °C, bp 120 °C (1 Torr)).

9-Vinylanthracene (9-VA), 9-methylanthracene (9-MeA) (Pfalz & Bauer), and 1-naphthol (BDH) were used as received. Methyl methacrylate monomer (MMA) (Eastman) was washed with NaOH and water, dried, and then distilled.

Polymers were prepared by free-radical polymerization in benzene solution degassed to <0.005 Torr residual pressure. Decanoyl peroxide was used as initiator. The choice of solvent and initiator was based on their low tendency to add fluorescing and quenching impurities to the polymer chain, compared to other common solvents and initiators. The PNMA–VA copolymer was polymerized to 20% yield for 9 h at 76 °C ($\overline{M}_n$ estimated from viscosity data is 2×10^5). The intrinsic viscosity $[\eta]$ of the copolymer in toluene at 30 °C is 0.146. The polymers were purified by multiple precipitation from benzene into methanol and were freeze dried from benzene. Further precipitation had no effect on the emission spectra. The concentration of 9-VA in the copolymers was determined by UV absorption at 380 nm (ϵ_{max} ~8000, PNMA–VA, 6% 9-VA in the feed, 0.06% 9-VA in the copolymer).

All solvents were Fisher reagent or spectroscopic grade. They were checked for residual emitting and absorbing impurities and were purified if necessary.

Steady state emission spectra were measured on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter and are shown uncorrected. Correction for nonideal response of the spectrofluorimeter was done by running several spectra in a fully corrected and in an uncorrected mode on a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter (courtesy of Xerox Research Centre of Canada Limited). The spectra were resolved and the necessary correction factor was found by comparing the relative contribution to the total emission of each component in the corrected and uncorrected spectra. Excitation was at 280 nm for naphthalene and at 360 nm for anthracene. Unless otherwise noted, all steady state and transient measurements were taken at 23 °C in 13 mm o.d. quartz tubing connected to a side arm. No fluorescence was observed from the grade of quartz used in these measurements. Samples were degassed by repeated freeze–thaw cycles on a vacuum line to a residual pressure of $<10^{-4}$ Torr.

Quantum yields of fluorescence ϕ_F were measured by comparing the area under the emission peak to the area under that of a sample of known quantum yield.

$$\frac{\phi_{F_2}}{\phi_{F_1}} = \frac{\text{area}_2\text{OD}_1\text{IF}_2 n_2^2}{\text{area}_1\text{OD}_2\text{IF}_1 n_1^2}$$

where OD is the optical density of the sample at 280 nm, IF is the correction for inner filter absorption, IF = 10^{Ad} where A is the optical density per centimeter and d is one-half the diameter of the cell, and n_1 and n_2 are the refractive indices of the pure solvents. 1-Naphthol (ϕ_F = 0.21) was used as standard, while 9-MeA (ϕ_F = 0.35) was used as secondary standard for the 1-

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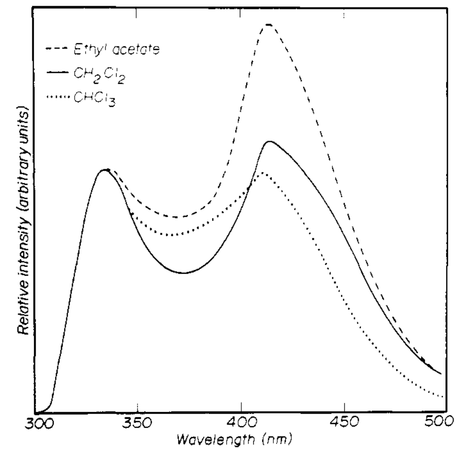


Figure 1. PNMA-VA fluorescence at 23 °C in several degassed solvents. Spectra normalized at 335 nm.

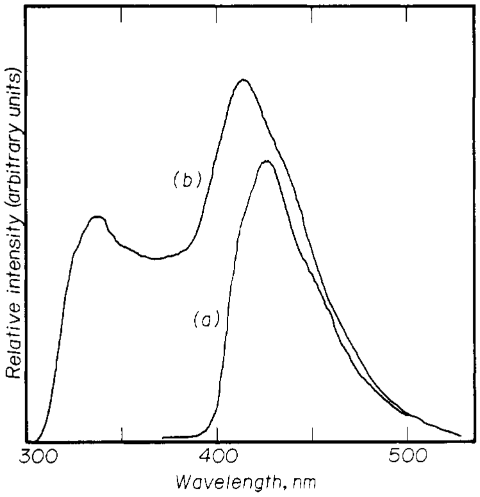


Figure 2. Fluorescence of (a) 9-VA (1.7×10^{-3} M) and (b) PNMA-VA at 23 °C in ethyl acetate.

naphthol. The accuracy of the inner filter correction was shown by the use of standards of different concentrations.

Lifetimes were measured by the technique of single photon time correlation on an instrument of standard design.[16-18] Various samples of known lifetime were run to check the correct operation of the instrument. With care, lifetimes in the region 1 to 10 ns could be obtained with a precision of better than ±0.5 ns.

Naphthyl chromophores were excited with a 280-nm interference filter (12-nm band-pass, Pomfret Research Optics). Anthracene-type chromophores were excited by a pair of filters, Corning 751 band-pass (310 to 410 nm) and Corning 0-51 cutoff (λ >380 nm). Thus a window from 380 to 410 nm was obtained.

Curves were resolved into their components by the use of a Du Pont 310 curve resolver. This instrument approximated each peak to a Gaussian distribution. Care must be taken in the interpretation of such results, since there may not be a unique solution if one or more peaks is poorly resolved in the original spectrum.

The polymers were fractionated in *n*-butyl acetate on a Bioglass column in a Waters Ana-prep gel permeation chromatograph. To overcome an interfering Raman line in the spectrum of *n*-butyl acetate, this solvent was removed and the fractionated polymer was examined in CH_2Cl_2.

UV absorption spectra were measured on a Cary 14 UV-visible spectrometer.

Results and Discussion

Table I
Fluorescence Lifetimes of Polymers and Model Compounds

system	ns	solvent
9-vinylanthracene	11.6 ± 0.5	ethyl acetate
9-methylanthracene	4.3 ± 0.5	cyclohexane
PNMA-VA	10.8 ± 0.5	cyclohexane

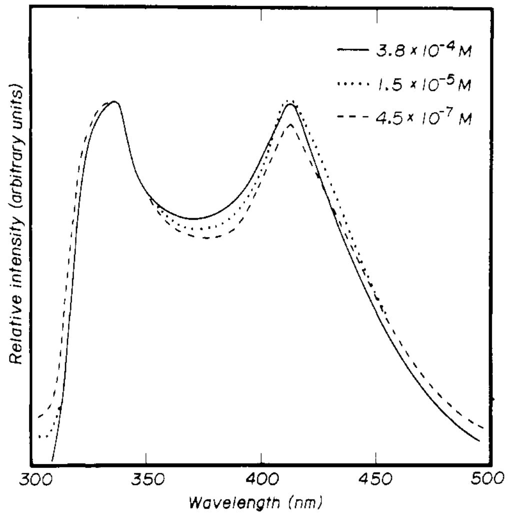


Figure 3. PNMA-VA fluorescence at 23 °C in CH_2Cl_2 as a function of concentration.

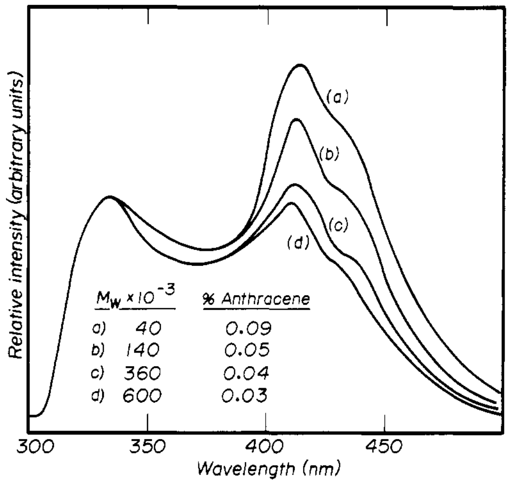


Figure 4. PNMA-VA fluorescence at 23 °C in aerated CH_2Cl_2 as a function of molecular weight. Spectra normalized at 335 nm.

In Figure 1 are shown the fluorescence emission spectra of PNMA-VA in $CHCl_3$, CH_2Cl_2, and EtOAc. The emission spectrum above 400 nm is very similar to the fluorescence emission of 9-VA (in EtOAc, Figure 2). The lifetime of the 420-nm emission in PNMA-VA in EtOAc is 10.8 ± 0.5 ns (excited at 380 nm), which is similar to the lifetime of 11.6 ± 0.5 ns for 9-VA in EtOAC (Table I). The lifetime of 9-MeA (Table I), however, is only 4.6 ± 0.5 ns, which is much less than the lifetime of the PNMA-VA copolymer or 9-VA. Furthermore, the emission from PNMA-VA does not show the structure characteristic of an alkyl-substituted anthracene (Figure 2). It seems likely, therefore, that the chromophore responsible for the emission of PNMA-VA above 400 nm is an intact 9-VA unit ($H_2C{=}CH$-anthracene). Further purification by multiple reprecipitation from benzene into methanol did not alter the relative intensity of the 9-VA emission, and fractional separation of the PNMA-VA copolymer by GPC did not significantly decrease the emission from 9-VA. Furthermore, if an amount of 9-VA greater than that present in the PNMA-VA copolymer (3×10^{-7} M at the PNMA concentrations employed) is added to PNMA solution, no emission from the 9-VA is observed. Also, the fluorescence spectra of PNMA-VA at several concen-

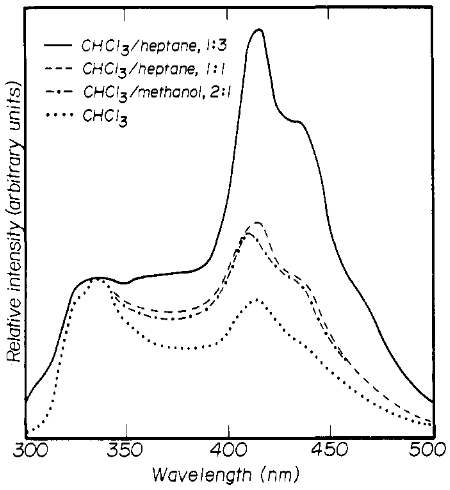
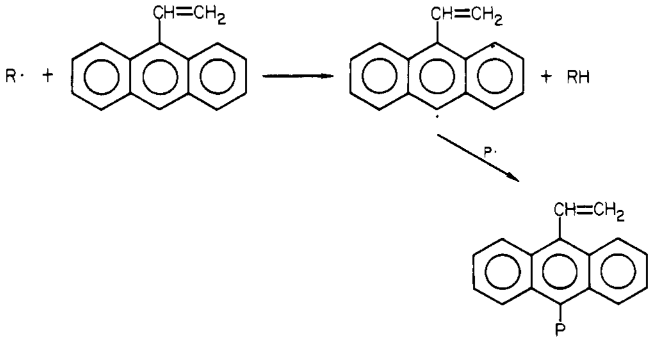


Figure 5. PNMA-VA fluorescence in degassed chloroform as a function of added nonsolvent. Spectra normalized at 335 nm.

trations (10^{-4}–10^{-7} M) are identical (Figure 3). Thus it can be safely concluded that the 9-VA is not free, but is attached intact to the polymer chain and that the energy transfer process is strictly intramolecular. Figure 4 shows the emission of the copolymer over a molecular weight range of 40 000 to 600 000, normalized to the same naphthalene monomer emission. The amount of 9-VA in each fraction is shown, and in each case works out to an average of slightly less than one 9-VA per polymer molecule. The 9-VA emission is greatest for the lowest molecular weight fractions, which have the highest anthracene concentrations. In at least one case,[19] polymers such as poly(methyl methacrylate) with anthracene units were prepared by a radical transfer process during polymerization using anthracene as a transfer agent. It seems reasonable that a similar process may account for the present results. The mechanism would probably involve the formation of a relatively stable free radical by removal of a proton from vinylanthracene, followed by termination by combination with a growing polymer chain:



where R· is either a primary or polymer radical and P· is a growing polymer radical.

The spectra in Figure 1 show maxima at 335 nm (naphthyl group emission) and at about 415 nm (9-VA emission). The relative intensity of the anthracene fluorescence is lowest in $CHCl_3$ and CH_2Cl_2, which are good solvents for the polymer. Both the naphthyl and the 9-VA emission are at a maximum in EtOAc, the poorest solvent. Similar effects are observed if a nonsolvent (polar, such as methanol, or nonpolar, such as cyclohexane or heptane) is added in increasing amount to one of the good solvents (Figure 5), showing again (as for PNMA homopolymer[19]) the observed intensity change with solvent is not a polar or dielectric effect. The chain contraction obtained as a result of the decrease in solvent power probably decreases the average donor–donor and donor–acceptor distance, thus increasing the probability of energy transfer.

Table II
Emission from PNMA-VA

solvent	$\phi_{F,total}$, ±10%	% naphthalene	% anthracene
$CHCl_3$	0.028	37	63
CH_2Cl_2	0.016	40	60
EtOAc	0.025	28	72

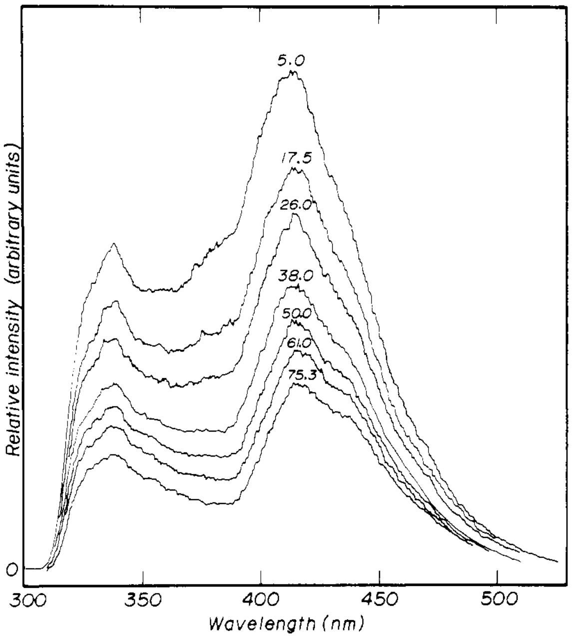


Figure 6. PNMA-VA fluorescence in degassed ethyl acetate as a function of temperature.

The normalized fluorescence at several concentrations is shown in Figure 3. These spectra confirm that energy transfer is intramolecular, between units of the same polymer molecule, since there is no effect of polymer concentration over at least two orders of magnitude.

At the concentration (2×10^{-7} M in 9-VA groups and 4×10^{-4} M in naphthyl groups) and excitation wavelength used, the direct absorption and emission by various model compounds (anthracene, 9-MeA, and 9-VA) is negligible. Therefore, virtually all of the 9-VA chromophore emission must be derived from energy transfer from naphthyl groups. Similarly, no anthracene-type emission was observed under these conditions in mixtures of 9-MeA or 9-VA with either PNMA or its small molecule model NIBA, so that radiative ("trivial") transfer from the naphthyl chromophore can also be excluded.

In Table II are shown the quantum yields of PNMA-VA fluorescence at 23 °C and a resolution of the spectra from Figure 1, corrected for instrumental response. Since the naphthalene excimer emission does not have a distinct maximum, the resolution can only be an approximation in which the emission is expressed as a percent of the naphthyl group (monomer plus excimer) and 9-VA fluorescence intensities. In all three solvents, more than 60% of the emission can be attributed to the anthracene moiety. Figure 6 shows the emission of the copolymer over a temperature range of 5.0 to 75.3 °C in ethyl acetate. As the temperature drops, the total quantum yield rises, but there is little change in the relative 9-VA/naphthyl intensity. However, at lower temperatures, a shoulder at 385 to 390 nm (naphthyl excimer emission) appears. The formation of excimer, as in the case of the PNMA homopolymer,[20] is highly dependent on temperature. Both the naphthyl and the 9-VA chromophore are equally affected

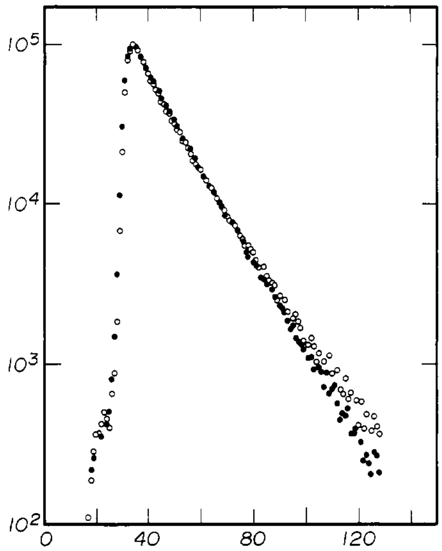


Figure 7. Fluorescence decay of PNMA-VA in chloroform irradiated at (○) 280 nm and (●) 380 nm, and viewing the 9-VA chromophore emission at 425 nm. Time setting, 0.65 ns/channel.

Table III
Molecular Weight and Lifetime Data for the PNMA-VA Copolymer (λ_{ex} 280 nm)

fluorescence lifetime, ns	mol wt	fluorescence lifetime, ns	mol wt
10.8	600 000	10.5	60 000
11.4	360 000	11.6	40 000
11.7	231 000	10.8	unfractionated[a]
11.2	140 000		

[a] λ_{ex} 380 nm.

by thermal quenching. Since thermal quenching is dependent upon the rate of solvent diffusion and the excited state lifetime, the fact that the ratio of the 9-VA group emission and the naphthyl monomer emission is constant (1.5 ± 0.5 from the ratio of peak heights from Figure 6) suggests that the two fluorescence bands arise from the same excited state, most likely the naphthyl chromophore.

In order to elucidate further the mechanism and efficiency of energy transfer from the initially excited naphthalene chromophore (when exciting at 280 nm) to the 9-VA unit in the PNMA-VA copolymer, fluorescence decays were measured using a Jarrell Ash monochromator to observe the emission at 425 nm, where 9-VA fluorescence occurs exclusively. In Figure 7 the decay of the 9-VA emission is shown upon excitation at either 280 nm where the naphthyl group absorbs exclusively or 380 nm where only the 9-VA chromophore absorbs. There is virtually no difference in the two decay spectra. Furthermore, the emission decay curves for the fractionated samples shown in Figure 4 are also identical within experimental error to those shown in Figure 7. Table III gives the fluorescence lifetimes for the PNMA-VA copolymer and its GPC fractions calculated from the best straight lines in the decay curve. It is thus concluded that the decay curve of the 9-VA chromophore emission is independent of both the exciting wavelength and the molecular weight (mol wt) of the polymer to which it is attached.

In order to gain some insight into the rate of energy transfer from the absorbing naphthyl chromophore to the 9-VA group attached to the chain, it is necessary to consider a rate law for formation and decay of the 9-VA chromophore excited state of the form:

$$I(t) = A_1(e^{-t/\tau_1} - e^{-kt}) \qquad (1)$$

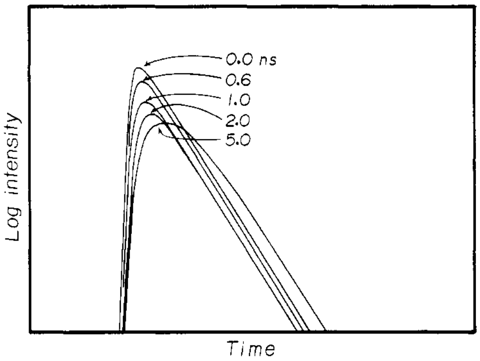


Figure 8. Theoretical variation of peak shape and position with times, $1/k$, required for energy transfer.

Equation 1 is identical to the equation given by Birks[21] for the decay curve of a liquid scintillation pulse of an acceptor molecule in the presence of an excited donor. $I(t)$ is the emission intensity of the 9-VA chromophore as a function of time, A_1 is a constant, and τ_1 is the measured lifetime of the 9-VA chromophore upon direct excitation at 380 nm. k is given by

$$k = k_0 + k_{tr} \qquad (2)$$

where k_0 is the reciprocal of the lifetime (τ_0) of the transferring state of the naphthyl chromophore and k_{tr} (which includes the relative concentration of acceptor) takes into account the average transfer rate of energy from the naphthyl chromophore to the 9-VA chromophore. Several decay curves (Figure 8) were calculated using eq 2 where τ_1 is 10.8 ns. At values of k corresponding to times ($1/k$) greater than 1 ns, the decay curves are shifted to longer times and the rising edges are rounded. At values of k corresponding to times less than 1 ns, the decay curves are virtually unchanged. Since it was shown (Figure 7) that the decay curve of the 9-VA chromophore excited at 280 nm (where naphthyl groups only absorb) was identical to the decay curve excited at 380 nm (where the 9-VA chromophore absorbs), the average time for transfer of energy from all absorbing naphthyl chromophores to the 9-VA group must be 1 ns or less.

The presence of emission of roughly equal intensity from the 1-naphthyl and 9-VA chromophores (Figure 1) suggests a comparable rate for energy transfer and naphthyl decay and both k_0 and k_{tr} must be of the order of 10^9 or greater. From the decay curve of PNMA emission,[20] the value of τ_0, the monomer lifetime emission of the naphthyl chromophore, can be estimated to be 1.5 ± 0.5 ns. Hence $k_0 = 0.7 \times 10^9$. Since k is greater than 10^9, then k_{tr} must be at least 0.7×10^9 and probably larger. Thus, 1.5 ± 0.5 ns is an upper estimate for τ_{tr}, the average time for energy transfer from the naphthyl to the 9-VA chromophore.

An important question raised by these experiments relates to the mechanism of the energy transfer process by which the excitation energy originally localized on the naphthyl chromophores is transferred to the anthracene group at the chain end. Does the energy migrate from naphthyl to naphthyl group until it reaches the vicinity of the anthracene, or does it transfer in a single step via the Förster mechanism?

The Förster R_0 value for transfer from monomeric naphthalene to anthracene chromophores is about 20 Å. From the intrinsic viscosity and molecular weight of the highest fractions of PNMA-VA shown in Figure 4, it is estimated that their root mean square end-to-end distance must exceed 100 Å, which would mean that most of the naphthalene units in the chain would be at a distance greater than the Förster radius. Since energy transfer is still quite efficient in the long chains, one may conclude that single-step Förster transfer is not an appropriate explanation, and one must postulate some kind of energy migration between naphthalene groups before the final transfer to anthracene. Whether or not this occurs by a "hopping" mechanism between adjacent naphthalenes or across loops in the chain cannot be established from these data, and a final resolution must await further experimental studies.

In conclusion it is evident from these results that the solvent exerts a significant effect on the energy transfer process from the naphthyl chromophores to the 9-VA trap in the PNMA–VA copolymer. This solvent effect cannot be attributed to dielectric or polar changes in the medium since addition of methanol (polar) or cyclohexane (nonpolar) to a solution of PNMA in $CHCl_3$ (a good solvent) decreases the excimer emission equally. Incorporation of a 9-VA trap into the naphthyl methacrylate polymer results in a very rapid (<1 ns) transfer or localization of energy on this chromophore, even when present at very low concentration (<0.06 mol %). The temperature dependence of the PNMA–VA fluorescence suggests a transfer of energy from the naphthyl monomer rather than the excimer. This rapid and efficient localization of energy from a network of absorbing naphthyl chromophores to a small concentration of low-energy traps is similar in many respects to the process of the energy localization process in aggregated systems and may simulate some of the aspects of photosynthesis.

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Singlet Oxygen Initiation of Polymer Photooxidation: Photolysis of *cis*-1,4-Poly(isoprene hydroperoxide)[1]

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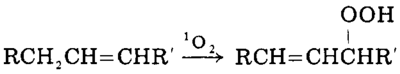
ABSTRACT: Reaction of singlet oxygen with *cis*-1,4-polyisoprene gives *cis*-1,4-poly(isoprene hydroperoxide). The kinetics and mechanism of the photolysis of this polymer–singlet oxygen adduct have been studied at 313 nm in solution in the absence of oxygen. The primary quantum yield for photolysis of the polymer hydroperoxide was 0.8. The subsequent radical-induced chain decomposition of the hydroperoxide results in a high overall quantum yield for hydroperoxide decomposition (Φ_{OOH}). The chain propagation reaction rate constant is estimated as 9×10^4 M^{-1} s^{-1}. The polymer degradation kinetics was studied and the rate constant for the β scission of the polymeric alkoxy radical (generated from primary hydroperoxide decomposition) is estimated as 2.7×10^4 s^{-1}. The quantum yield of polymer chain scission (Φ_S) is of the order of 0.1. From the experimental values of Φ_{OOH} and Φ_S, the ratio Φ_S/Φ_{OOH} can be approximated as a constant of 0.014. This agrees remarkably well with the theoretical value of 0.01 derived from the mechanism proposed in this study.

The detailed mechanism and kinetics of the initiation of elastomer photooxidation is still an open question.[2] One proposed mechanism involves the addition of singlet molecular oxygen to form an allylic hydroperoxide in general polymers as a key preinitiation step.[3] The subsequent photodecomposition of this hydroperoxide would initiate an autocatalytic chain reaction.[4] The reaction of singlet oxygen with olefinic acceptor systems has been studied extensively.[5-9] The addition of singlet oxygen to the double bonds of an unsaturated polymer to give an allylic hydroperoxide attached to the polymer chain proceeds via the well-known "ene" reaction mechanism:[10]



$$RCH_2CH{=}CHR' \xrightarrow{^1O_2} RCH{=}CH\overset{OOH}{C}HR' \qquad (1)$$

In order to understand the detailed mechanism of the photooxidation of elastomers in general, and the role of singlet oxygen in the initiation step in particular, it is important to investigate the kinetics and mechanism of

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