

Fluorescence Studies of Photo-Cross-Linkable Poly[vinyl 3-(1- and 2-naphthyl)acrylate-co-vinyl hexanoate-co-vinyl acetate] and Its Model Compounds

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ABSTRACT: The intramolecular 2 + 2 photocycloaddition of ethylene bis[3-(1- and 2-naphthyl)acrylates] (1E and 2E), the intermolecular 2 + 2 photodimerization of ethyl 3-(1- and 2-naphthyl)acrylate (1ET and 2ET), and the photo-cross-link reaction of poly[vinyl 3-(1- and 2-naphthyl)acrylate-co-vinyl hexanoate-co-vinyl acetate] (P(V1NA-co-VH-co-VA) and P(V2NA-co-VH-co-VA)) have been studied in methylene chloride (and films for polymers). After 2 + 2 photocycloaddition or photodimerization, new fluorescence bands from naphthalene monomer and excimer were found from these systems. The naphthalene excimer is made up of two naphthalene rings bonded to two cyclobutane ring carbons in 1,2 or 1,3 positions, and on the same side of the cyclobutane ring. Photo-cross-link reactions for P(V1NA-co-VH-co-VA) and P(V2NA-co-VH-co-VA) are much faster compared to their small-molecule analogue systems (1ET and 2ET).

Introduction

A new class of photopolymers, which has found wide application in photoresists, photolithography, and UV-curable resins, is based on 2 + 2 cyclodimerization of olefinic groups bonded to polymeric backbones. The naphthylacrylates provide an example for such cross-linkable polymers. Photoisomerization and photodimerization of naphthylacrylate have already been studied,¹⁻³ and the photochemistry of its polymer analogues has also been reported in a patent.⁴ The fluorescence behavior, however, was not discussed there and remains obscure.

In this paper the fluorescence responses of poly[vinyl 3-(1- and 2-naphthyl)acrylate-co-vinyl hexanoate-co-vinyl acetate] and their model compounds, i.e., ethyl 3-(1- and 2-naphthyl)acrylate and ethylene bis[3-(1- and 2-naphthyl)acrylates], have been studied in solution and in a polymer matrix. Possible new excimer geometries are discussed.

Experimental Section

Materials. 3-(1- and 2-naphthyl)acrylic acids were synthesized by the Knoevenagel condensation⁵ from the corresponding naphthaldehyde and recrystallized from ethanol. The melting point was 212 °C (lit.⁶ mp 210 °C) for 3-(1-naphthyl)acrylic acid and 211 °C (lit.⁵ mp 209 °C) for 3-(2-naphthyl)acrylic acid.

Ethyl esters (1ET and 2ET) were obtained by mixing the corresponding acrylic acid chloride and dry ethanol in toluene with a trace amount of pyridine. The melting point was 36.5–37.5 °C for ethyl 3-(1-naphthyl)acrylate (1ET) and 62–63 °C for ethyl 3-(2-naphthyl)acrylate (2ET). Similarly, ethylene bis[3-(1-naphthyl)acrylate] (1E) and ethylene bis[3-(2-naphthyl)acrylate] (2E) were synthesized from the corresponding acid chloride and ethylene glycol but at a slightly elevated temperature. The melting point was 118–120 °C (lit.² mp 114–115 °C) for 1E and 151–152 °C (lit.² mp 148 °C) for 2E.

¹H NMR (200-MHz) spectra (ppm) for the compounds are as follows: 1ET, 1.38 (t, 3 H, methyl), 4.32 (q, 2 H, methylene), 6.53 (d, 1 H, *J* = 15.7, α -vinyl), 7.25–8.22 (m, 7 H, aromatic), 8.52 (d, 1 H, *J* = 15.7, β -vinyl); 2ET, 1.36 (t, 3 H, methyl), 4.29 (q, 2 H, methylene), 6.55 (d, 1 H, *J* = 16.0, α -vinyl), 7.26–7.93 (m, 8 H, aromatic and β -vinyl). The ¹H NMR spectra for 1E and 2E are in agreement with those from Tanaka et al.²

Figure 1 shows the UV absorption spectra of 1ET, 2ET, and 2-(1-naphthyl)ethyl acetate in methylene chloride solution.

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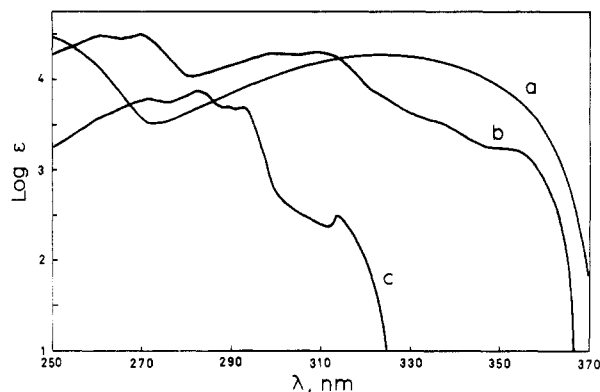


Figure 1. UV absorption spectra of (a) ethyl 3-(1-naphthyl)acrylate, (b) ethyl 3-(2-naphthyl)acrylate, and (c) 2-(1-naphthyl)ethyl acetate in methylene chloride.

Poly(vinyl alcohol) (87–89% hydrolyzed; catalog no. 36,317-0, lot no. 06804TW) was purchased from Aldrich; the sample had an average molecular weight of 13 000–23 000. The esterification of poly(vinyl alcohol) followed the method described in ref 4. For example, 1.5 g of polymer was suspended in 40 mL of pyridine at 60 °C for 16 h. The suspension was cooled to 50 °C, and 3 g of 3-(1-naphthyl)acryloyl chloride was added. The reaction mixture was then stirred at 50 °C for 12 h, followed by 4 h at 75 °C. The reaction mixture was cooled to 50 °C again, and an excess amount (3 g) of hexanoyl chloride was added. The solution was warmed at 50 °C for 6 h, followed by 6 h at 75 °C. The amber, viscous solution was cooled and filtered, then precipitated by the addition of water, washed with methanol, and finally dried under vacuum at room temperature. In this manner, the poly[vinyl 3-(1-naphthyl)acrylate-co-vinyl hexanoate-co-vinyl acetate] obtained had a chromophore modification degree of 0.45. The chromophore modification degree is the ratio of the number of moles of chromophore used in the modification to the number of moles of poly(vinyl alcohol) based on the calculated average molecular weight (49) for its monomeric unit. The purpose of adding hexanoyl chloride is to increase the solubility of the resultant polymer in methylene chloride.

A proton NMR spectrum of a sample having a stoichiometric composition of 9.1% was run in order to check the modification degree. The NMR method gave a value of $8.3 \pm 0.8\%$. We assume that the modification degrees calculated in this work have similar accuracy.

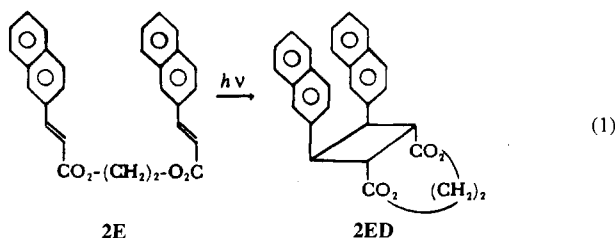
Film Preparation. Thin films were prepared by spin coating from methylene chloride solution at 5000 rpm on 22-mm-diameter Suprasil disks (Hellma), using a Model EC 101D photoresist spinner (Headway Research, Garland, TX). Other films were prepared by solution casting.⁷

Irradiation Techniques. Polymer films were irradiated following the method described in ref 7. Solutions were sealed in a $1 \times 1 \times 4$ cm³ quartz cell with a septum cap and then purged with nitrogen, after which the method from ref 7 was followed.

Spectroscopic Techniques. A Varian DMS UV-visible spectrophotometer was used for UV absorption measurements on both solutions and polymer films. The fluorescence spectra of model compounds and polymers were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorometer and are shown uncorrected for the wavelength dependence of the detector response. All emission spectra, except those in Figure 7, were excited on 287 nm with an emission spectral bandwidth of 2 nm. Most excitation bandwidths were 4 nm, except for those otherwise specified. The fluorescence lifetime was measured by single-photon-counting⁷ and was analyzed by iterative reconvolution.⁸ The solvent ethyl acetate (ACS spectrophotometric grade; Aldrich) was used without further purification.

Results and Discussion

Model Compound Fluorescence. On UV irradiation of a solution of 2E, a photodimerization reaction should occur. According to Tanaka et al.,² the photochemical reaction of 2E is a rapid intramolecular 2 + 2 cycloaddition of 2E accompanied by a slow trans-cis isomerization, giving a single product, 2ED, as shown in reaction 1. In reaction 1, the 2 + 2 photocyclization is suprafacial;



trans-2E will yield 2ED with two naphthalene groups on the same side of the cyclobutane ring (if a planar conformation is assumed). Although cyclobutane is non-planar, the probability of forming a coplanar excimer conformation for two naphthalene groups is much larger for example than it would be for 1,2-dinaphthylethane. Note that in such an excimer configuration the chromophore distance will be much shorter than 3 Å if all the carbons in the naphthalene rings still retain sp² hybridization.

Parts a and b of Figure 2 show typical fluorescence spectra accompanying 330–370-nm irradiation of 1.70×10^{-5} M 2E in methylene chloride. Pure *trans*-2E solution (without UV irradiation) has an emission spectrum with a maximum at ca. 390 nm; with brief irradiation, the relative fluorescence intensity at 390 nm decreased rapidly (for irradiation times up to 30 s), and a shoulder began to emerge (for 90 s) at wavelengths between ca. 320 and 360 nm. Figure 2b shows the fluorescence spectra of the same sample for longer irradiation times under the same conditions, except that the excitation bandwidth has been changed from 4 nm (Figure 2a) to 10 nm (Figure 2b). The peaks between 320 and 360 nm can be associated with naphthalene chromophores, as can be judged from their structure. The peak with a maximum at 390 nm decreases continuously but slowly with irradiation time. This peak reaches its minimum intensity after 10 min of irradiation, then rises slowly in intensity (15 min), and eventually achieves a maximal intensity after 25 min of irradiation. Further irradiation causes the relative intensity of the peak at 390 nm to decrease (not shown) but has a weaker effect on the structured peak in the 320–360-nm range.

The observed change of the relative fluorescence intensity at 390 nm can probably be explained in the

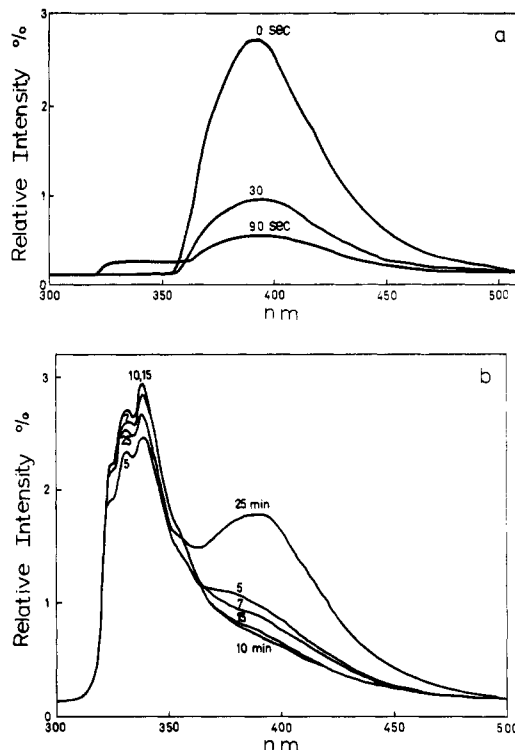


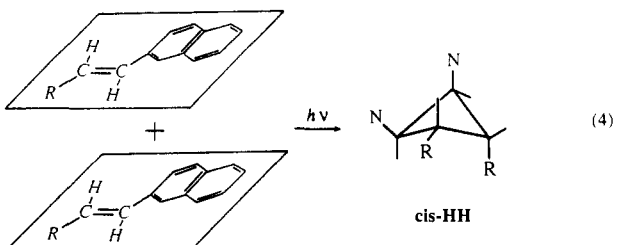
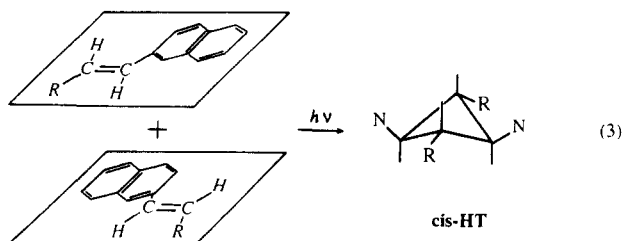
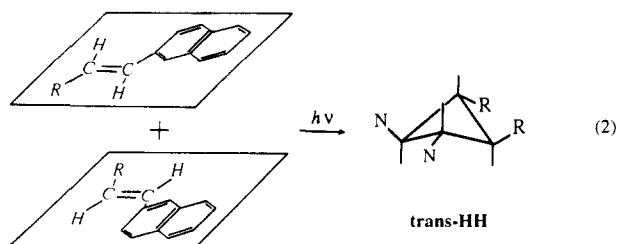
Figure 2. Variation of fluorescence spectra with time of irradiation at 330–370 nm for 1.70×10^{-5} M 2E in methylene chloride with excitation spectral bandwidths of (a) 4 nm and (b) 10 nm.

following way. The fluorescence signals for 2E and for naphthalene excimers are almost coincident at 390 nm. No excimer fluorescence for 2E is observed.² While the trans-cis isomerization of 2E is a slow, competitive reaction of reaction 1 and the fluorescence quantum yield for *cis*-2E is very small,² the *cis* isomer nonetheless acts, like *trans*-2E, as an energy quencher for the naphthalene monomer excited state and the naphthalene excimer. Therefore, the peak intensity at 390 nm decreases rapidly at first, because dimerization proceeds very rapidly, the rate of decrease then slows down due to (a), the decreased reactant concentration in eq 1, and (b), quenching of the naphthalene excimer fluorescence by 2E. The gradual increase in intensity which occurs at later times can be accounted for by increased naphthalene excimer fluorescence, which occurs as the 2E (*trans* and *cis*) concentration drops. Finally, prolonged irradiation causes the fluorescence signals to decrease, likely due to photocycloaddition between naphthalene chromophores, as has been characterized by Kamijo et al.⁹

Irradiation of 2ET will not give a single product. According to Tanaka et al.,² photodimerization of ethyl 3-(1- and 2-naphthyl)acrylate is a singlet process. In this concerted reaction, the HOMO of the excited state overlaps with the LUMO of the ground state to form a cyclobutane. Since the 2 + 2 photodimerization via a singlet excited state is suprafacial, the substituents on the double bond have not changed relative positions in the product. If reactions are induced by triplet sensitization, the photodimerizations of ethyl 3-(1-naphthyl)acrylate will proceed by a two-step mechanism,^{3,10} which involves formation of a triplet biradical, followed rapidly by inversion of the electron spin to close the ring. The triplet-state configurational change from the ground state is immeasurably small for ethyl 3-(1-naphthyl)acrylate, since conjugation involves a large aryl ring.³ In both cases, the stereochemistry of products can probably be deduced from molecular

models, since the configurations of the reaction intermediate have not been altered. Note that this is likely not true for cinnamate, which has large configurational changes between the ground and triplet states.^{3,11}

In our experiment the photodimerizations proceed by a singlet excited state,² so that the reactions have higher quantum yields than they would have had if they had proceeded via a triplet state.¹⁰ As shown by eqs 2–4, head-



to-head photodimerization of *trans*-2ET will yield cyclobutane derivatives with naphthalene groups on different sides of the ring (*trans*-HH), so that they are unable to show excimer fluorescence. Head-to-tail addition, however, will give rise to cyclobutane derivatives with naphthalene groups on the same side of the ring (*cis*-HT), so that they can be expected to form excimer structures. The *cis*-HH product, which involves an addition mode similar to that for 2ED, is estimated in the literature³ to occur with a 5% yield. Since *trans*-*cis* isomerization is a very slow reaction for 2ET, dimerization contributions from the *cis* isomer can be neglected. In these equations, R denotes CO₂C₂H₅ and N represents the naphthyl group.

To maximize reactions 2–4 and minimize the *trans*-*cis* isomerization, 13 h of 330–370-nm irradiation was carried out on a concentrated solution (1.87×10^{-2} M) of 2ET in methylene chloride under nitrogen. Fluorescence and UV spectra were measured in dilute solution. Figure 3 shows the relative intensities of the fluorescence, with different spectra for different concentrations recorded under exactly the same conditions. Except for the naphthalene monomer fluorescence maximum at ca. 340 nm, there are stronger excimer fluorescence peaks at 390 nm. Table I lists the ratio of fluorescence intensities at 390 nm to those at 340 nm for solutions having different concentrations. The value decreases slightly with increasing initial chromophore concentration; this phenomenon is likely caused by the quenching effect of residual *cis*- and *trans*-2ET. This fluorescence ratio should increase with an increase in the total chromophore concentration were the excimers formed between two different molecules. The

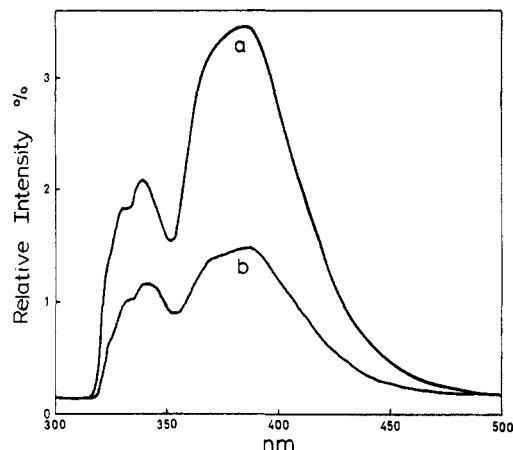


Figure 3. Fluorescence spectra for 1.87×10^{-2} M 2ET in methylene chloride after 13 h of 330–370-nm irradiation and diluted to (a) 3.72×10^{-4} M and (b) 8.93×10^{-4} M initial chromophore.

Table I
Ratio of Naphthalene Excimer to Monomer Emission
Intensities at Different Concentrations^a

[total chromophore], ^b M	I_{390}/I_{340}
1.08×10^{-5}	2.02
3.72×10^{-4}	1.73
8.93×10^{-4}	1.32

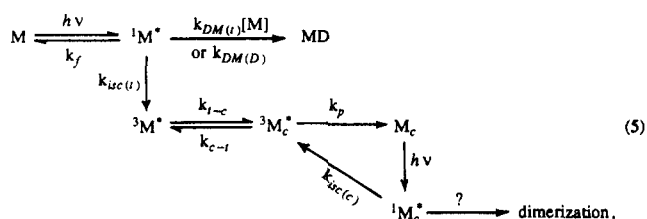
^a For experimental conditions, see Figure 3. ^b Concentration of the total chromophore including the concentration of 2ET and different dimers. In calculation, a dimer is equivalent to two 2ET.

concentration-independent excimer-to-monomer fluorescence intensity ratio provides evidence that the chromophores forming the excimers are indeed bonded to the same molecule.

We have also observed structured fluorescence peaks for 2E or 2ET cyclohexane solutions, similar to those in Figure 1 of ref 2.

Photochemical reactions of 1E and 1ET have been carried out in different solvents. Since the reactions are rapid *trans*-*cis* isomerization, followed by a slow photodimerization,² we can only obtain mixtures of the *cis* isomer and dimers. For example photodimerization of 2.32×10^{-2} M 1ET in methylene chloride under air was conducted by 44.5 h of 330–370-nm irradiation, because the quantum yield for dimerization is greater in air than in argon.² The fluorescence measurements have the ratio $I_{393}/I_{340} = 2.77$ in nitrogen, compared to the ratio $I_{400}/I_{340} = 1.43$ in air; it is apparent that the excimer is more easily quenched by oxygen; note that its maximum is 7 nm red-shifted in the presence of oxygen.

According to Tanaka et al.,² the following scheme can be used to summarize the photoprocesses involved in this work:



In this scheme M_c denotes the *cis* monomer, M denotes the *trans* monomer, and a superscript asterisk indicates an excited state, while left superscripts 1 and 3 represent singlet and triplet states. Further, k_t , k_p , k_{t-c} , k_{c-t} , $k_{isc(t)}$, $k_{isc(c)}$, $k_{DM(t)}$, and $k_{DM(D)}$ represent rate constants for

fluorescence, phosphorescence, trans-to-cis isomerization, cis-to-trans isomerization, intersystem crossing of a trans isomer, intersystem crossing of a cis isomer, dimerization from the trans isomer, and dimerization from the trans bichromophoric molecule, respectively, while MD is the product of the photodimerization step.

Although our primary interest is not in trans-cis isomerization and the photochemical behavior of *cis*-2ET, *cis*-1ET, *cis*-2E, and *cis*-1E, the contribution to photodimerization from *cis*-2ET can be estimated roughly from published data, if we neglect the difference between methyl and ethyl groups. The radiative lifetime can be evaluated from the approximate relationship (6)¹²

$$\tau_0 \approx 10^{-4} / \epsilon_{\max} \quad (6)$$

where ϵ_{\max} is the molar extinction coefficient at maximum wavelength, τ_0 is in seconds, and ϵ_{\max} is in L mol⁻¹ cm⁻¹. The fluorescence lifetime τ can be calculated from eq 7 where q_f is the fluorescence quantum yield. By using data

$$\tau = q_f \tau_0 \quad (7)$$

from ref 2 we have determined the lifetime for *trans*-2Me in methanol to be $\tau_{\text{trans-2Me}} = 1.55$ ns and the lifetime for *cis*-2Me in methanol to be $\tau_{\text{cis-2Me}} = 0.27$ ns. Therefore, the ratio $\tau_{\text{trans-2Me}}/\tau_{\text{cis-2Me}}$ is 6. In addition the concentration of the cis isomer is very small compared with that of the trans isomer in our experiments, and the dimerization contributions from the cis isomer can thus be neglected. There are no data available which can be used to evaluate the photodimerization contributions from *cis*-1ET. It is possible that some *cis*-1ET will take part in the dimerization reaction and thereby generate dimers other than those in eqs 3–5. However, those new dimers which are able to produce excimer fluorescence should be similar to *cis*-HT and *cis*-HH, except that the relative positions of R can be changed from equatorial to axial, and vice versa.

The quantum yield of dimerization of 2E is about 25 times that of 1E in deoxygenated solvents.² Since this dimerization proceeds via a singlet excited state, these differences suggest that the lifetime of the singlet state for 2E is much longer than that for 1E. Figure 4 illustrates the fluorescence decay measurements for 2E. Since photodimers are also able to fluoresce, a longer excitation wavelength (350 nm) has been chosen deliberately. Carefully purified 2E in ethyl acetate gave rise to single-exponential decay of the fluorescence, with a lifetime of 3.8 ns, as shown by the decay curve of Figure 4. No excimer fluorescence of 2E was detected by the single-photon-counting technique. We were unfortunately unable to measure the lifetime for 1E, because the decay data almost overlapped the instrument response function.

Polymer Fluorescence. Figure 5 shows UV absorbance changes with different irradiation times for poly-[vinyl 3-(1-naphthyl)acrylate-co-vinyl hexanoate-co-vinyl acetate] (P(V1NA-co-VH-co-VA)) with a chromophore modification degree of 0.16 and a total chromophore concentration of 4.87×10^{-5} M in methylene chloride. The decrease in the absorbance at 326 nm is accompanied by an increase in the absorbance at 286 nm, which is relevant to the loss of the 3-(1-naphthyl)acrylate chromophore and the gain of the naphthalene chromophore, as can be deduced from examining the UV spectrum of 2-(1-naphthyl)ethyl acetate in Figure 1. The corresponding fluorescence spectra are shown in Figure 6. Surprisingly, the fluorescence intensities at 400 nm emitted from ethyl 3-(1-naphthyl)acrylate decreased with irradiation time very

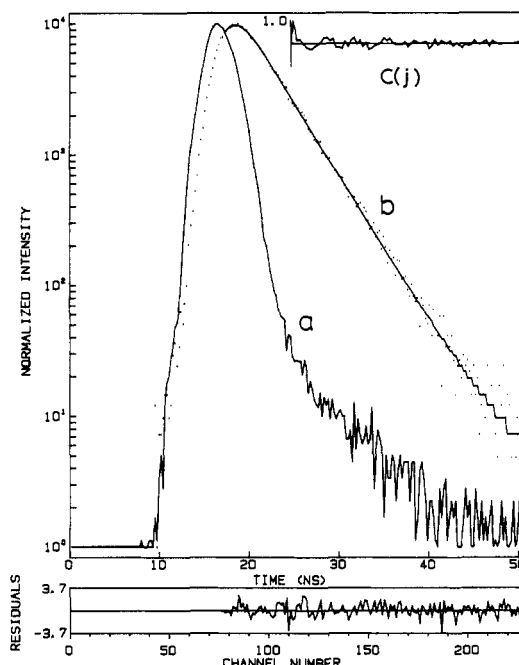


Figure 4. Fluorescence decay of 1.23×10^{-4} M 2E in ethyl acetate; $\lambda_{\text{ex}} = 350$ nm, $\lambda_{\text{em}} = 383$ nm. Curve a: instrument response function at 440 nm. Curve b: points, experimental data; solid line, best-fit reconvolution with instrument response function. The reduced χ^2 is 1.17. C(j) is the autocorrelation function of the weighted residuals.⁸

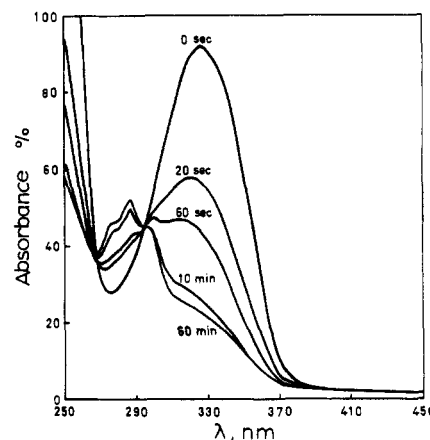


Figure 5. UV absorbance changes accompanying 330–370-nm irradiation of P(V1NA-co-VH-co-VA) in methylene chloride with a chromophore modification degree of 0.16 and a total chromophore concentration of 4.87×10^{-5} M.

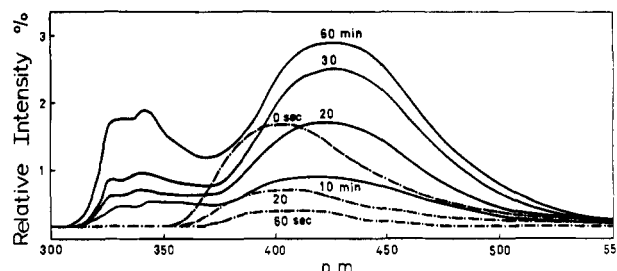


Figure 6. Fluorescence spectra of the deoxygenated polymer solution described in Figure 5.

rapidly, following which the monomer and excimer fluorescences from the naphthalene chromophore appeared. These peaks simultaneously increased with increasing irradiation time; note that it requires a much greater irradiation time to obtain equivalent monomer and excimer fluorescence from corresponding small chro-

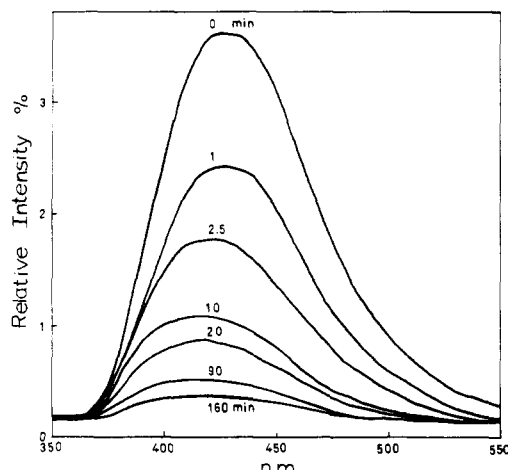


Figure 7. Variation of the fluorescence intensity with time of irradiation at 330–370 nm for a P(V1NA-co-VH-co-VA) film. The chromophore modification degree is 0.48.

mophore systems. It seems that once 1E or 1ET is bonded to a polymer chain, the trans-cis isomerization is mostly eliminated, so that photodimerization can proceed without difficulty. Since the chromophore modification degree is 0.16, there are not many neighboring 3-(1-naphthyl)acrylate chromophore pairs in the modified poly(vinyl alcohol) before irradiation, so that the most probable photodimerization mode is from the head-to-tail chromophore pairs bonded to different macromolecules or to different segments of the same macromolecule. Photodimerization from this mode will give rise to the *cis*-HT product, in a manner similar to that described by eq 3. For the *cis*-HT product with the naphthalene groups separated by three cyclobutane carbons, the distance separating the chromophores is close to 2.2 Å if we assume a planar cyclobutane ring and sp^2 hybridization for the naphthalene carbons. This geometry appears to favor the formation of the excimer conformation. The only difference is that the excimer fluorescence in Figure 6 is red-shifted by about 30 nm from that appearing in Figure 3: this red-shift is partly associated with the different substitution pattern in the naphthalene rings. Excimer fluorescence bands for α -substituted naphthalene polymers, as reported in the literature, range from 390 nm^{13,14} to 420 nm.^{15,16}

It is generally accepted that the lowest-energy excimer configuration corresponds to a planar sandwich configuration with maximum overlap of the aromatic rings. A distance of 3 Å is estimated for the naphthalene excimer on the basis of pressure experiments,^{17,18} and a thickness of 3.2 Å is assigned to the aromatic rings.¹⁹ If sp^2 hybridization is assumed for the naphthalene carbons and a planar conformation is assumed for the cyclobutane ring, unrealistic distances of 1.54 Å (*cis*-HH) and 2.2 Å (*cis*-HT) are deduced for these excimers. Therefore, two bent σ bonds might be involved in these excimer configurations.

Different fluorescence spectra were observed for the same polymer when cast on quartz disks rather than in solution. Figure 7 demonstrates the relative intensities of fluorescence changes with irradiation for a P(V1NA-co-VH-co-VA) film with a chromophore modification degree of 0.48. The fluorescence signals, which were excited at 340 nm, can only emit from 3-(1-naphthyl)acrylate chromophores. The maximum fluorescence intensities are at 428 nm, 28 nm red-shifted by comparison to 400 nm in solution (see Figure 6). Although the monotonic decrease of the fluorescence intensity with irradiation time suggests that dimerization proceeds smoothly, the slower intensity decrease with increasing irradiation time means

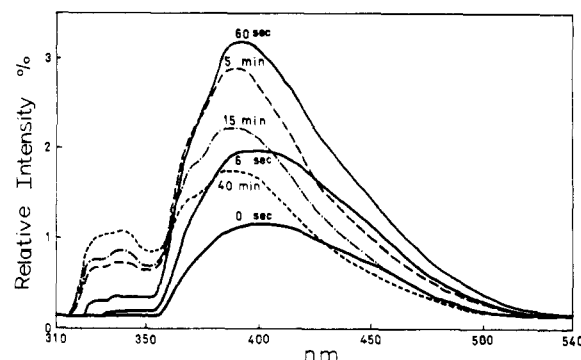


Figure 8. Variation of fluorescence spectra with time of irradiation at 330–370 nm for P(V2NA-co-VH-co-VA) in methylene chloride, with a chromophore modification degree of 0.58 and a total chromophore concentration of 1.70×10^{-4} M.

that the probability of finding a neighboring 3-(1-naphthyl)acrylate decreases due to the consumption of adjacent pairs of initial chromophores, leaving only isolated initial chromophores in the films. The same emission spectra are obtained by setting the excitation maximum at 287 nm, which is the maximum absorption band of the naphthalene chromophores. Fluorescence of naphthalene monomers can be removed by long-term extraction of the less cross-linked polymer films (the less cross-linked polymer film was separated from the quartz disk, then swelled in methylene chloride for several days, and finally filtered for measurements).

These experimental facts suggest that it is unreacted residual chromophores and their *cis* analogues which de-excite the excited state of the naphthalene groups in modified P(V1NA-co-VH-co-VA) films, because of the shorter distances between chromophores in polymer films.

Similar phenomena have been observed for P(V1NA-co-VH-co-VA) films with a chromophore modification degree of 0.16.

Figure 8 shows the fluorescence spectrum changes that occur with irradiation for poly[vinyl 3-(2-naphthyl)acrylate-co-vinyl hexanoate-co-vinyl acetate] (P(V2NA-co-VH-co-VA)) with a chromophore modification degree of 0.58 and a total chromophore concentration of 1.70×10^{-4} M in methylene chloride. The shoulders at ca. 370 nm suggest that the excimer fluorescence may be a combination of two components. Since the concentration is large, both adjacent and nonadjacent chromophore dimerizations are possible. Dimerization is so rapid that a few second of irradiation causes completion of the dimerization of almost all adjacent pairs, and 1 min of irradiation has already initiated some nonadjacent chromophore dimerizations. The isolated initial chromophores have been exhausted after about 15 min of irradiation, as can be seen from the intensity decrease at longer wavelengths and from the shifts of the maxima to shorter wavelengths.

The decrease of the relative intensity for long-time irradiation is probably caused by photocycloaddition between naphthalene chromophores⁹ bonded to different dimers. This is consistent with the manner in which the monomer intensities have changed in opposite directions.

Conclusions

Excimer emission, a characteristic phenomenon of many aromatic chromophores, has been studied in naphthalene compounds and polymers bearing naphthalene chromophores. Hirayama's work¹⁹ established that the contribution to the total fluorescence spectra from excimers is greatest when the chromophores are separated by three atoms (the so-called $n = 3$ rule). When $n = 2$, there are

no conformations available to the molecule which will allow a coplanar arrangement of the aromatic rings, whereas, for $n > 3$, the probability of finding such coplanar conformations is so small that it can be neglected.²⁰

Our results show that, as an exception, once naphthalene chromophores are bonded to the same side of a cyclobutane ring, there is a possibility of fluorescence. If they are at the 1 and 2 positions on the cyclobutane ring, then the excited state will likely be depopulated by further cyclization between the naphthalene rings; if they are at the 1 and 3 positions on the cyclobutane ring, excimer fluorescence is predominant and a decrease of fluorescence intensity with irradiation is not very apparent in our experiments.

The excimer is formed by two naphthalene rings separated by three (or even two) cyclobutane ring carbon(s) at the cost of generating two bent (distorted) σ bonds. Strong sp^2 - sp^3 σ bonds are not possible for excimers of *cis*-HT (eq 3) and *cis*-HH (eq 4), because if this is so, it will not be possible to form a coplanar conformation for the naphthalene rings. The energy increase due to two distorted σ bonds can be well compensated by the formation of a lower energy excimer configuration. The possibility for a naphthalene ring to find another ring is thus increased by rotation restriction of the bonds between the two naphthalene rings because of the cyclobutane ring structure.

Similar phenomena can be expected to be observed if the naphthalene ring is replaced by benzene or anthracene rings.

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References and Notes

- (1) Tanaka, H.; Honda, K.; Suzuki, N. *J. Chem. Soc., Chem. Commun.* 1977, 506.
- (2) Tanaka, H.; Takamuku, S.; Sakurai, H. *Bull. Chem. Soc. Jpn.* 1979, 52, 801.
- (3) Herkstroeter, W. G.; Farid, S. *J. Photochem.* 1986, 35, 71.
- (4) Daly, R. C.; Engebrecht, R. H. Canadian Pat. 1106544, 1981.
- (5) Fulton, J. D.; Robinson, R. *J. Chem. Soc.* 1939, 200.
- (6) Rona, P.; Feldman, U. *J. Chem. Soc.* 1958, 1737.
- (7) Wang, Z.; Holden, D. A.; McCourt, F. R. W. *Macromolecules* 1990, 23, 3773.
- (8) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1984.
- (9) Kamijo, T.; Irie, M.; Hayashi, K. *Bull. Chem. Soc. Jpn.* 1978, 51, 3286.
- (10) Reiser, A. *Photoreactive Polymers*; Wiley: New York, 1989; p 85.
- (11) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; Wiley: New York, 1987; p 416.
- (12) Nishijima, Y. *Prog. Polym. Sci. Jpn.* 1973, 6, 199.
- (13) Holden, D. A.; Rendall, W. A.; Guillet, J. E. *Ann. N.Y. Acad. Sci.* 1981, 366, 11.
- (14) Holden, D. A.; Guillet, J. E. *Macromolecules* 1982, 15, 1475.
- (15) Holden, D. A.; Guillet, J. E. *Development in Polymer Photochemistry*; Applied Science Publishers: Barking, U.K., 1980; Vol. 1.
- (16) Holden, D. A.; Safarzadeh-Amiri, A.; Sloan, C. P.; Martin, P. *Macromolecules* 1989, 22, 315.
- (17) Braun, H.; Förster, T.; Bunsenges, B. *Phys. Chem.* 1966, 70, 1091.
- (18) Braun, H.; Förster, T. *Z. Phys. Chem. (Munich)* 1971, 78, 40.
- (19) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, U.K., 1985.
- (20) Klöpffer, W. *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1973; Vol. 1.