

# Photophysical Processes in Polymers. VII. Electronic Energy Migration and Trapping in Alternating Copolymers

Robert B. Fox,\* Thomas R. Price, Robert F. Cozzens,<sup>1</sup> and William H. Echols

Naval Research Laboratory, Washington, D. C. 20375. Received August 12, 1974

**ABSTRACT:** Emission spectra of films and dilute solutions at 77 and 293°K are used in a study of electronic energy migration and trapping in poly(styrene-*alt*-methyl methacrylate), poly(2-vinylnaphthalene-*alt*-methyl methacrylate), poly(styrene-*alt*-2-naphthyl methacrylate), and poly[(styrene-*co*-2-vinylnaphthalene)-*alt*-methyl methacrylate], synthesized *via* the ethylaluminum sesquichloride complex. Related homopolymers and random copolymers are also investigated. Excimer formation is not observed in the alternating copolymers in good solvents, in  $\theta$  solvents, or in films; both nonnearest-neighbor and interchain-excimer interactions are therefore absent in these systems. Charge-transfer interaction between aromatic chromophores and adjacent ester carbonyl groups on the same chain is suggested as the basis for chromophore separation and the lack of excimer-forming interaction in the alternating systems. Incorporation of traps in the copolymers is used to show that intrachain triplet migration in alternating copolymers is as facile as it is in the corresponding homopolymers, indicating that conditions are far less restrictive for migration than for excimer formation. Sequences of a few methyl methacrylate units are sufficient to inhibit triplet migration through aromatic groups on the same chain, but interchain migration in solid films is still possible. Depending on location within a solid alternating polymer system, a few adventitious low-energy impurities can be the locus for delayed exciplex or delayed excimer formation under conditions where excimers themselves are not readily formed.

Intrachain interaction between a chromophore in the excited singlet state and a chromophore in the ground state to yield an excimer is commonly encountered in vinylaromatic and vinylheterocyclic polymers. Excimers can be formed intramolecularly through adjacent chromophores on a chain, as in polystyrene or the poly(vinylnaphthalenes),<sup>2,3</sup> or between nonnearest neighbors as in the case of poly(1-naphthyl methacrylate)<sup>4</sup> or poly(acenaphthalene).<sup>3,5</sup> Triplet excimer formation has been observed in poly(*N*-vinylcarbazole)<sup>6</sup> and its 3,6-dibromo analog.<sup>7</sup>

Energy levels of excimer states are lower than those of the corresponding singlet or triplet excited states. Excimer sites thus can act as traps for energy migrating along a polymer chain and will compete with other types of traps in the same chain for the migrating energy. Likewise, further transfer of trapped energy to an acceptor in the system is complicated by the possibility of energy transfer from an excimer in competition with other donor sources. To separate these phenomena, a system is desirable in which ener-

gy migration and trapping is possible in the absence of excimer formation. Dilute solutions of polymers such as polystyrene in glasses at 77°K are such systems,<sup>2,3</sup> but the corresponding solid polymers at 77°K still show excimer fluorescence because the solids are formed at a temperature where excimer sites exist.<sup>3</sup>

Mikawa and coworkers<sup>8</sup> observed only carbazole group molecular fluorescence over a wide range of temperatures in alternating copolymers from *N*-vinylcarbazole and comonomers such as fumaronitrile or diethyl fumarate. The corresponding random copolymers are not available in these systems, but excimer fluorescence is observed in the *N*-vinylcarbazole homopolymer and some of its copolymers containing low concentrations of units derived from styrene or vinyl acetate.<sup>9</sup> If nearest-neighbor interaction is the effective excimer-forming process, as it is in poly(*N*-vinylcarbazole),<sup>9</sup> and if the conditions for excimer formation are more restrictive than those for intrachain energy migration, alternating copolymers should offer a vehicle for the study of migration and trapping in the absence of excimer formation. With this in mind, we have investigated alternating copolymer systems derived from methyl or 2-naphthyl methacrylate and a second monomer containing an aromatic ring.

## Experimental Section

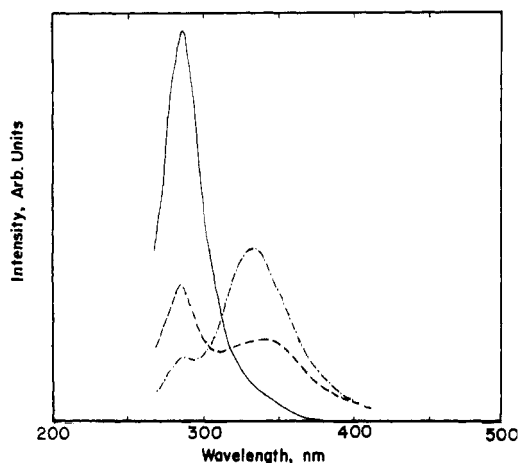
Alternating copolymers were synthesized by the standard procedure of adding by syringe a solution of 0.066 mol of ethylaluminum sesquichloride (as a 1.54 *M* solution in *n*-heptane) to a stirred solution of 0.075 mol of ester (methyl methacrylate or 2-naphthyl methacrylate) in 50 ml of dry toluene under helium at -78°. After 15 min, 0.12 mol of styrene, 2-vinylnaphthalene, or the appropriate mixture of these monomers, and 0.006 mol of benzoyl peroxide in 18 ml of toluene were added and the mixture was stirred 15 min at -78° and 1 hr at room temperature. The resulting mixture was taken up in methylene chloride and precipitated into a methanol-HCl mixture. Further purification was made by precipitation into cyclohexane followed by three or more reprecipitations into methanol and drying under vacuum for 24 hr. Homopolymers and random copolymers were prepared by conventional methods in degassed benzene solutions at 60° with azobisisobutyronitrile as the initiator; these polymers were purified by 4–5 reprecipitations from methylene chloride or tetrahydrofuran into methanol.

The polymers and their analysis are given in Table I. Ultraviolet absorption spectra were used for analysis. The resulting compositional data are approximate, since they are based on the measured extinction coefficients of polystyrene at 259 nm and of poly(2-vinylnaphthalene) and poly(2-naphthyl methacrylate) at 319 nm,

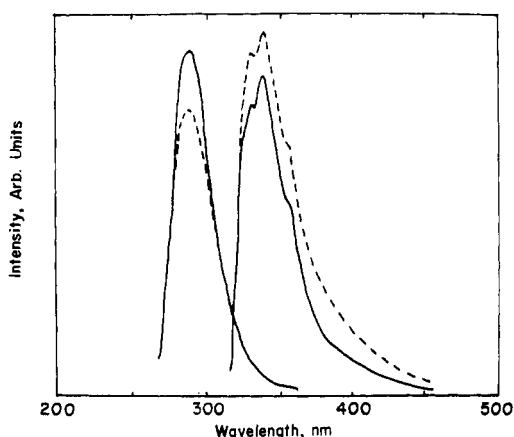
**Table I**  
Polymers and Copolymers<sup>a</sup>

Material	Composition, mol %			
	S units	2VN units	MMA units	2NMA units
P(S- <i>alt</i> -MMA)	52		48	
P(S- <i>co</i> -MMA) (1:1) <sup>b</sup>	50		50	
PS	100			
P(2VN- <i>alt</i> -MMA)		52	48	
P(2VN- <i>co</i> -MMA) (1:99)		0.7	99.3	
P2VN		100		
P(S- <i>co</i> -2VN) (97:3)	95	5		
P[(S- <i>co</i> -2VN)- <i>alt</i> -MMA]	47	1.5	51.5	
P(S- <i>co</i> -2VN- <i>co</i> -MMA) (49:2:49)	56	2	42	
P(S- <i>co</i> -2VN- <i>co</i> -MMA) (94:3:3)	90	4	6	
P(S- <i>alt</i> -2NMA)	44			56
P2NMA				100

<sup>a</sup> S = styrene, 2VN = 2-vinylnaphthalene, MMA = methyl methacrylate, 2NMA = 2-naphthyl methacrylate. <sup>b</sup> Monomer feed ratios are given in parentheses.



**Figure 1.** Fluorescence spectra of styrene polymers and copolymers at 293°K, 0.04 mg/ml in 1:1 tetrahydrofuran-diethyl ether (T/E),  $\lambda_{\text{ex}}$  260 nm: P(S-alt-MMA) (—), P(S-co-MMA) (---), PS (- · -). In this and subsequent figures, the relative intensities of the various spectra are not comparable since incident intensities at the sample varied slightly from run to run.



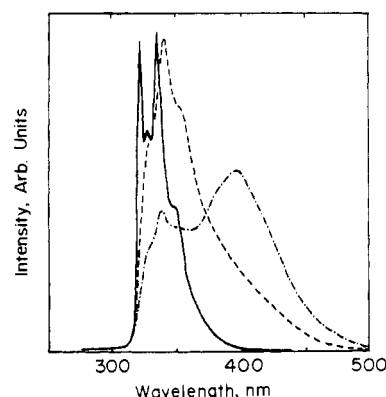
**Figure 2.** Fluorescence spectra ( $\lambda_{\text{ex}}$  260 nm) of alternating copolymers at 293°K,  $10^{-3}$  M (Ar units) solutions in methylene chloride (—) and in the methylene chloride-cyclohexane  $\theta$  solvent (---): P(S-alt-MMA) spectra on the left, P(2VN-alt-MMA) spectra on the right.

and there is no assurance that the extinction coefficients of the chromophores in the copolymers have corresponding values. Indeed, this method of analysis has been questioned in the case of styrene copolymers.<sup>10,11</sup> The ultraviolet absorption spectra for our copolymers from styrene and methyl methacrylate were found to be similar to those reported for styrene-acrylonitrile copolymers,<sup>11</sup> with an almost complete elimination of the absorption for polystyrene at 269 nm in the alternating copolymer.

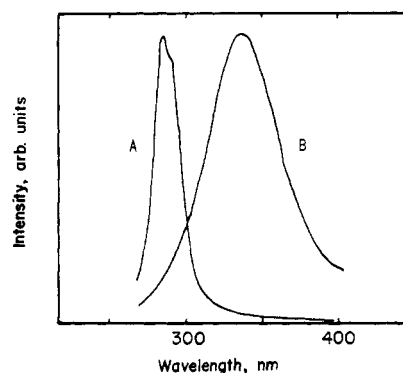
Emission spectra, measured with an Aminco-Bowman spectrofluorimeter utilizing a 1P28 photomultiplier, are uncorrected for instrument response. Procedures and materials, other than the polymers and copolymers, were generally those given in previous papers in this series.<sup>3,12</sup>

## Results

**Prompt Emission.** Fluorescence spectra of dilute solutions of P(S-alt-MMA) at room temperature are compared in Figure 1 to the spectra of random P(S-co-MMA) (1:1) and of PS itself. Over the temperature range  $-146$  to  $25^\circ$ , no change other than in overall intensity is observed in the P(S-alt-MMA) spectrum. Since the latter fluorescence corresponds closely to that of model compounds such as toluene, it is clear that excimer formation in P(S-alt-MMA) is not detectable under these conditions. Further, a random copolymer of essentially the same composition does show



**Figure 3.** Total emission spectra ( $\lambda_{\text{ex}}$  260–290 nm) of T/E solutions,  $10^{-3}$  M (2NMA units): P2NMA or P(S-alt-2NMA), 77°K (—); P(S-alt-2NMA), 293°K (---); P2NMA, 293°K (- · -).



**Figure 4.** Fluorescence spectra of films at 293°K,  $\lambda_{\text{ex}}$  260 nm: A, P(S-alt-MMA); B, PS.

some excimer emission under the same conditions, indicating that sequences of S units are present in the chain.

Analogous results are obtained with P(2VN-alt-MMA) solutions at room temperature, as shown in Figure 2. The fluorescence at 340 nm is similar to that observed in naphthalene and its derivatives and in a MMA copolymer containing 1% 2VN; the fluorescence does not correspond to the excimer fluorescence at 400 nm seen with P2VN. Figure 2 also shows that nonnearest-neighbor interaction to form excimers is not detectable under  $\theta$  conditions with either P(S-alt-MMA) or P(2VN-alt-MMA). These spectra were obtained from methylene chloride solutions to which cyclohexane had been added just to the point of opalescence.

The case of P(S-alt-2NMA) is of special interest because of the possible excited state interactions between adjacent phenyl and naphthyl groups on the same chain. Analysis based on absorption spectra suggests that the alternating copolymer may contain a few short sequences of 2NMA units or that traces of P2NMA are present. Excimer formation as observed in P2NMA may therefore occur to a small extent in P(S-alt-2NMA), as shown in Figure 3, but no change is observed when the spectrum is run with the alternating copolymer in a  $\theta$  solvent. Dilute solutions of P2NMA have the same prompt emission spectra at room temperature in methylene chloride, ethyl acetate, and in the  $\theta$ -solvent mixture of methylene chloride and cyclohexane. Therefore, nonnearest-neighbor interaction to form excimers is absent in P2NMA, even though it has been observed in P1NMA.<sup>4</sup> The fluorescence in the 340-nm region appears to be naphthyl group molecular fluorescence, since S-unit excimers are not expected on the basis of the results with P(S-alt-MMA), and the total emission spectra at

**Table II**  
**Delayed Emission Spectra at 77°K,  $\lambda_{\text{ex}}$  260 nm**

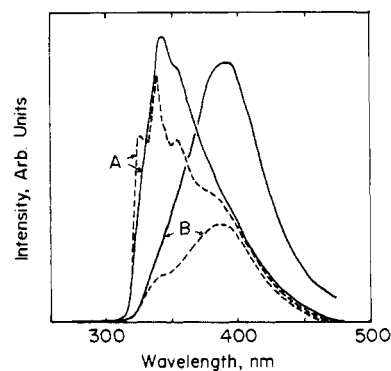
Material	Phase <sup>a</sup>	Major $\lambda_{\text{max}}$ , nm	$\tau_{\text{em}}$ , sec <sup>b</sup>
P(S- <i>alt</i> -MMA)	s	392	4.0
	f	405	2.3
P(S- <i>co</i> -MMA) (1:1)	s	392	2.5
	f	426	NE
PS	s	390	3.5
	f	430	NE
P(2VN- <i>alt</i> -MMA)	s	490, 524	1.9
		338 (B) <sup>c</sup>	NE
	f	524	<0.4
		366 (B)	NE
P(2VN- <i>co</i> -MMA) (1:99)	s	476, 506	3.0
	f	484, 514	2.5
P2VN	s	486, 520	2.0
		335 (B)	NE
	f	534	NE
P(S- <i>alt</i> -2NMA)	s	486, 516	2.0
		335 (B)	0.5
	f	522	NE
P2NMA	s	483, 515	2.0
		340 (B)	NE
	f	522	NE
P(S- <i>co</i> -2VN) (97:3)	s	476, 508	3.1
	f	480, 516	2.0
P[(S- <i>co</i> -2VN)- <i>alt</i> -MMA]	s	474, 506	3.1
	f	482, 510	2.4
P(S- <i>co</i> -2VN- <i>co</i> -MMA) (49:2:49)	s	474, 508	3.0
		390 <sup>d</sup>	2.5
	f	483, 514	2.0
P(S- <i>co</i> -2VN- <i>co</i> -MMA) (94:3:3)	s	471, 504	3.1
	f	488, 520	2.0

<sup>a</sup> s = solution,  $10^{-3}$  M in 2VN units or 2NMA units or, for S-MMA copolymers, S units; f = film. <sup>b</sup> NE = nonexponential decay. <sup>c</sup> (B) = biphotonic emission; all other  $\lambda_{\text{max}}$  are monophotonic. <sup>d</sup> No emission with  $\lambda_{\text{ex}}$  290.

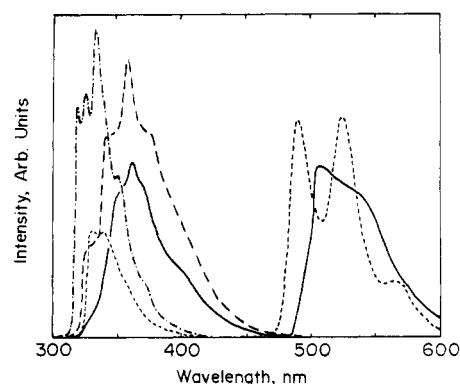
77°K of P(S-*alt*-2NMA) and P2NMA are identical. The almost complete absence of S-unit molecular fluorescence in P(S-*alt*-2NMA) at 77°K or at room temperature is probably a consequence of the filtering effect of the strongly absorbing naphthyl groups.

Opportunities for interchromophore interaction should be maximized in a solid polymer; both intra- and interchain interactions are possible. Excimer fluorescence is primarily observed with films of PS or P2VN at room temperature. In contrast, the room temperature prompt emission from a P(S-*alt*-MMA) film, shown in Figure 4, consists solely of molecular fluorescence identical with that observed in dilute solution. Results with P(2VN-*alt*-MMA) are somewhat different, in that the major fluorescence maximum is shifted to 365 nm in the film, and the band is sufficiently broad that it overlaps the region of P2VN excimer fluorescence observed at about 425 nm in films. No positive indication of excimer emission from films of P(2VN-*alt*-MMA) is observed, however. Films of P(S-*alt*-2NMA) at room temperature (Figure 5) show essentially the same molecular fluorescence as in dilute solution, but the broadening in the 400-nm region is somewhat greater in the film than in solution.

Prompt fluorescence spectra from solutions and films of all three alternating copolymers at 77°K are generally simi-



**Figure 5.** Total emission spectra of films at 293°K (—) and 77°K (---): A, P(S-*alt*-2NMA); B, P2NMA.



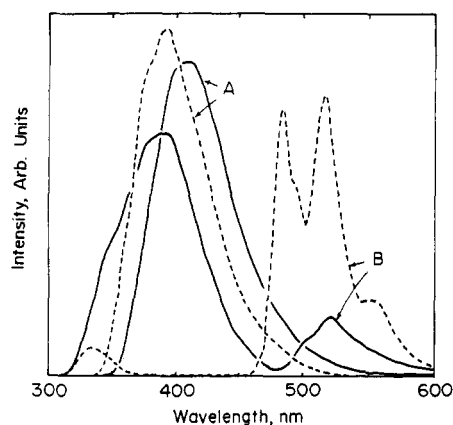
**Figure 6.** Emission spectra of P(2VN-*alt*-MMA) at 77°K,  $\lambda_{\text{ex}}$  290 nm: films, delayed (—) and total (---);  $10^{-3}$  M (2VN units) in T/E, delayed (- · -) and total (· · ·).

lar to those observed at room temperature, except that the overall intensities are greater at the lower temperature. Phosphorescence is much more evident in the total emission at 77°K from dilute solutions of P(S-*alt*-NMA) (F/P ~ 2) and P(2VN-*alt*-MMA) (F/P ~ 30) than it is in PS or P2VN (F/P ~ 100).

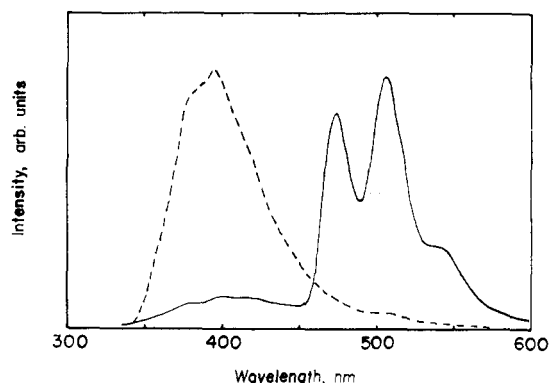
**Singlet Energy Transfer.** A comparison of room-temperature fluorescence spectra from spectrally equivalent dilute solutions of P[(S-*co*-2VN)-*alt*-MMA] and a mixture of P(S-*alt*-MMA) and P(2VN-*co*-MMA) (1:99) shows that relative to the mixture, the intensity of fluorescence at 280 nm (from S units) is lower and the fluorescence at 340 nm (from 2VN units) is greater in P[(S-*co*-2VN)-*alt*-MMA], indicating that transfer is more efficient in the terpolymer than in the mixture. However, no separation could be made of the processes of trivial reabsorption and radiationless energy transfer in this system.

**Delayed Emission.** Delayed emission spectra of dilute solutions and films of P(S-*alt*-MMA), P(S-*alt*-2NMA),<sup>13</sup> and P(2VN-*alt*-MMA) are given in Figures 6 and 7. Major delayed emission band maxima and lifetimes for these and related polymers appear in Table II. Intensities of bands indicated to be biphotonic in origin are approximately proportional to the square of the intensity of the exciting light and are therefore presumed to result from triplet-triplet annihilation processes of the type encountered in P1VN.<sup>12</sup>

**Triplet Migration and Trapping.** The alternating copolymer from styrene and methyl methacrylate in which a few S units have been replaced in a random manner by 2VN units provides a demonstration of migration and trapping in this type of polymer chain structure. As shown in Figure 8, in a dilute solution of P[(S-*co*-2VN)-*alt*-MMA] the phosphorescence originates almost entirely from the naphthyl groups. The intrachain nature of the migration is



**Figure 7.** Delayed emission spectra at 77°K,  $\lambda_{\text{ex}}$  260 nm, for films (—) and  $10^{-3}$  M (S units) T/E solutions (---): A, P(S-*alt*-MMA); B, P(S-*alt*-2NMA).



**Figure 8.** Delayed emission spectra at 77°K,  $\lambda_{\text{ex}}$  260 nm, for a 0.4 mg/ml solution in T/E: P[(S-*co*-2VN)-*alt*-MMA] (—) and a spectrally matched mixture of P(S-*alt*-MMA) and P(2VN-*co*-MMA) (1:99) (---).

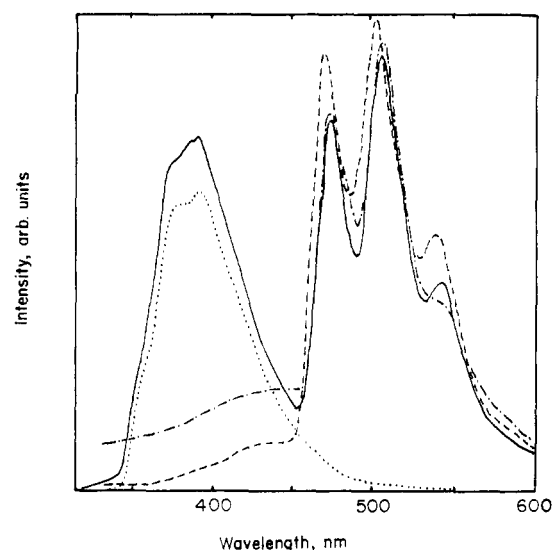
further supported by comparison with the spectrum of a spectrally equivalent mixture of P(S-*alt*-MMA) and P(2VN-*co*-MMA) (1:99), in which the phosphorescence is almost entirely from S units.

Energy migration and trapping by 2VN units are also highly efficient processes in a random copolymer of styrene with only a few per cent of MMA and 2VN units in each chain, as seen in Figure 9. However, this is not the case with the random terpolymer P(S-*co*-2VN-*co*-MMA) (49:2:49). Although the composition of this random terpolymer is similar to P[(S-*co*-2VN)-*alt*-MMA], much of the triplet energy is not trapped by 2VN units but is emitted by S units. Thus, since migration and trapping is very efficient in both solutions and films of P[(S-*co*-2VN)-*alt*-MMA] and P(S-*co*-2VN-*co*-MMA) (94:3:3), but is efficient only for films (see Table II) of P(S-*co*-2VN-*co*-MMA) (49:2:49), interchain energy migration must occur in the latter polymer and very likely occurs in the former polymers as well.

Inspection of Table II shows that polymers having 2VN units in which triplet energy is localized have similar naphthyl group phosphorescence maxima and lifetimes in dilute solutions. In contrast, polymers in which triplet energy is delocalized through naphthyl groups in either 2VN or 2NMA units have naphthyl group phosphorescence maxima shifted to longer wavelengths (*i.e.*, lower energy levels) and have significantly shorter lifetimes.

## Discussion

In the diphenylalkanes, intramolecular excimer formation is observed only when the phenyl groups are separated



**Figure 9.** Delayed emission spectra at 77°K,  $\lambda_{\text{ex}}$  260 nm, for 0.4 mg/ml in T/E solutions of random copolymers: P(S-*co*-2VN-*co*-MMA) (49:2:49) (—); P(S-*co*-2VN-*co*-MMA) (94:3:3) (---); P(2VN-*co*-MMA) (1:99) (-.-.); P(S-*co*-MMA) (1:1) (···).

by a chain of three carbon atoms, allowing a stable face-to-face arrangement of benzene rings having a separation distance of 2.54 Å.<sup>14</sup> For 1,5-diphenylpentane, the most stable alkane chain configuration is the extended trans form, which leads to a phenyl-phenyl separation distance of over 5 Å, too great for excimer formation.<sup>14</sup> It has been estimated that excimer formation is possible for benzene rings in a parallel conformation with a separation of 3.73 Å or less.<sup>2</sup>

Molecular models for PS and P(S-*alt*-MMA) indicate that the same argument may be used to explain the lack of excimer-forming sites in the alternating copolymer. The models also indicate that in the extended trans conformation, the carbonyl group in P(S-*alt*-MMA) is sufficiently close to a nearest-neighbor benzene ring for interaction, perhaps charge transfer in nature, that would tend to maintain the extended conformation and the separation of rings from each other. Charge-transfer complexes between S and MMA may be involved in the synthesis of P(S-*alt*-MMA), and ionic cyclization reactions in which the ester carbonyl group becomes bonded to the ortho position of an adjacent benzene ring have been carried out in both P(S-*alt*-MMA)<sup>15</sup> and P(S-*co*-MMA).<sup>16</sup> Ultraviolet absorption spectra suggest a different ground state involving the aromatic ring in the alternating copolymer relative to the homopolymer. The same type of spectral change has also been observed in copolymers of styrene and polar monomers such as maleic anhydride or acrylonitrile but not in styrene copolymers with butadiene.<sup>11</sup>

Structural characterization of highly alternating copolymers has usually been made by nuclear magnetic resonance techniques. Emission spectroscopy provides an additional tool for characterization, as indicated by the spectra of the compositional pairs P(S-*alt*-MMA) and P(S-*co*-MMA) (1:1) in Figure 1 and P[(S-*co*-2VN)-*alt*-MMA] and P(S-*co*-2VN-*co*-MMA) (49:2:49) in Figures 8 and 9. In the random copolymer of the former case, excimers are formed by nearest-neighbor interaction, demonstrating the presence of short S-unit sequences. In the second example, triplet trapping at the 2VN units is less efficient in the random terpolymer because of the interruption of the intrachain migration process by sequences of MMA units.

The high efficiency of excimer formation at room temperature in dilute solutions of aromatic homopolymers

such as PS<sup>17</sup> or P1VN<sup>2</sup> has been cited in support of efficient delocalization of singlet energy in these polymers. Our results do not provide direct evidence for singlet delocalization in P(S-*alt*-MMA) or P(S-*alt*-2NMA); in the latter case, the absence of S-unit fluorescence may be due to radiative transfer to the naphthyl groups. The interchromophore separations and conditions, quite restrictive for excimer formation, are far less restrictive for migration. Migration by an electron-transfer process can occur over distances up to about 15 Å,<sup>18</sup> and such distances have been verified for migration of triplet energy in the P(1VN-*co*-S) system.<sup>12</sup> In P(2VN-*alt*-MMA), singlet energy migration to traps intrinsic to a few chains does take place in films but not in solutions at both room temperature and at 77°K. The fluorescence is monophotonic and it resembles that of 2-naphthaldehyde.

Triplet energy migration and trapping appears to be as efficient in the alternating systems as in the corresponding homopolymers. Ketonic impurities that function as triplet-trapping sites in PS<sup>19</sup> were not observed in P(S-*alt*-MMA) films. Incorporation of a few 2VN units in this system, in P(S-*co*-MMA) containing only a few MMA units, or in PS itself resulted in polymers exhibiting triplet emission almost entirely from the 2VN traps. In the random terpolymer, P(S-*co*-2VN-*co*-MMA), having essentially the same composition as the alternating system, trapping was incomplete in solution. It is concluded that intramolecular triplet energy migration cannot span the distance interposed by a sequence of several MMA units in the polymer chain. The possibilities of triplet energy hopping a single MMA unit or migrating by way of the combined S-MMA unit have not been separated in the present work.

The 1VN<sup>12</sup> and 2VN copolymer systems are of special interest because of the apparent trap emission observed as fluorescence or delayed fluorescence at about 360 nm in films, but not in solutions, of copolymers having more than about 30% VN units. This emission is not observed in copolymers with a low proportion of VN units, in P1VN, or in P2VN, and the result is the same with either styrene or methyl methacrylate as the comonomer with 1VN or 2VN. With the exception of P(2VN-*alt*-MMA), the copolymers also show a delayed biphotonic emission in the 400–450-nm region and a broad delayed monophotonic emission in the 520-nm region; both of these emissions also occur in solid P1VN and P2VN. The spectrum of the alternating system is shown in Figure 6; in this spectrum, no 400–450-nm delayed emission is apparent.

These results can be interpreted<sup>12</sup> in terms of a competition for migrating photon energy by traps in a few chains and many excimer-forming sites fixed in the film at room temperature at the time of preparation. The traps have not been identified other than to note a resemblance of their spectra to those of 2-naphthaldehyde. Trap fluorescence (and delayed fluorescence) occurs at about 360 nm (see Figure 6) and phosphorescence occurs as a single broad band near 520 nm. Delayed emission in the 400–450-nm region will depend on the proximity of a 2VN unit to the trapping site in the copolymer.

As the proportion of comonomer units in the 2VN or 1VN chain increases, the probability of forming nearest-neighbor excimer sites and the probability of electronic energy migration will both decrease in the random copolymer series. In films, extreme cases are represented by the following. (1) The homopolymer, P2VN, in which migration and excimer formation are both maximized and triplet-triplet annihilation at the trap gives delayed excimer or delayed exciplex fluorescence at 410 nm. (2) The alternating copolymer, P(2VN-*alt*-MMA), in which migration is highly

efficient and excimer formation is minimized. Singlet migration to the trap leads to trap fluorescence, and triplet-triplet annihilation at the trap leads only to delayed trap fluorescence because the process  $T_1 + T_1^g \rightarrow S_1 + S_0^g$ , where g represents a guest trap, leads to species too far apart to form an excimer. (3) The polymer having isolated 2VN units, represented by P(2VN-*co*-MMA) (1:99), in which both migration and excimer formation are minimized and where film and solution spectra will be similar. (4) The isolated 2VN-unit polymer, represented by P(S-*co*-2VN) (97:3) or P[(S-*co*-2VN)-*alt*-MMA], in which migration occurs with the 2VN unit acting as a trap, and excimer formation involving 2VN units does not occur. The delayed emission is that of the 2VN traps and, in appearance, it resembles that of case 3.

The biphotonic delayed emission observed at about 390 nm in P2NMA films may be delayed excimer fluorescence, as in case 1, but if the excited singlet resulting from annihilation is  $S_1^g$ , its interaction with an adjacent ground state 2NMA unit would be properly termed delayed exciplex fluorescence. This emission is nearly identical with that from films of P(S-*alt*-2NMA), where a trap could replace either an S or a 2NMA unit. The excited singlet resulting from annihilation may be  $S_1^g$  or  $S_1$  from the adjacent S or 2NMA unit, but interaction with any adjacent group would necessarily lead to a delayed exciplex emission. Alternatively, the trap is the same in both P2NMA and the copolymer, and the emission in the 390-nm region is delayed trap fluorescence that coincidentally appears in the region of excimer fluorescence.

It is clear that the detailed chemical structure of a polymer chain is all important in determining the nature and relative importance of the radiative and nonradiative photophysical processes occurring in polymer systems. The relationship between polymer structure and subsequent photochemical processes such as photodegradation is under study and will be the subject of future communication from this laboratory.

## References and Notes

- (1) Department of Chemistry, George Mason University, Fairfax, Va. 22030.
- (2) M. T. Vala, Jr., J. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).
- (3) R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, **57**, 534 (1972).
- (4) A. C. Somersall and J. B. Guillet, *Macromolecules*, **6**, 218 (1973).
- (5) C. David, M. Piens, and G. Gueskens, *Eur. Polym. J.*, **8**, 1019 (1972).
- (6) W. Klöpffer and D. Fischer, *J. Polym. Sci., Part C*, **40**, 43 (1973).
- (7) M. Yokoyama, M. Funaki, and H. Mikawa, *Chem. Commun.*, 372 (1974).
- (8) (a) Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, *Macromolecules*, **7**, 4 (1974); (b) M. Yoshimura, Y. Shirota, and H. Mikawa, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 457 (1973).
- (9) K. Okamoto, A. Yano, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jap.*, **47**, 749 (1974).
- (10) S. Russo and B. M. Gallo, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **15**(1), 90 (1974).
- (11) R. J. Brüssau and D. J. Stein, *Angew. Makromol. Chem.*, **12**, 59 (1970).
- (12) R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, **57**, 2284 (1972).
- (13) The biphotonic delayed emission near 390 nm in films of P(S-*alt*-2NMA) and P2NMA at 77°K decays slowly under illumination in the spectrometer; the phenomenon, which is reversible, is being further investigated.
- (14) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
- (15) N. G. Gaylord, B. K. Patnaik, and Z. Janovic, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 203 (1973).
- (16) N. Grassie, J. Gilks, T. Moodie, P. Quietsch, and P. Riordan, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2287 (1973).
- (17) F. Hirayama, L. J. Basile, and C. Kikuchi, *Mol. Crystallogr.*, **4**, 83 (1968).
- (18) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N.Y., 1970.
- (19) G. A. George, *J. Appl. Polym. Sci.*, **18**, 419 (1974).