

SELECTED ASPECTS OF PHOTOCHEMISTRY IN POLYMER MEDIA

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Abstract - A number of selected aspects of the reciprocal interactions of polymers with excited solutes or polymer-bound chromophores are given. The role of free volume, glass-transition temperature (T_g), microscopic viscosity, and polarity or environments to which excited molecules are exposed is emphasized in order to illustrate possible manners in which the photophysical, photochemical, and subsequent chemistries can be influenced.

Many of these factors can affect several monomolecular and bimolecular processes encountered in the sensitization of photocrosslinkable polymers: the photophysics of the sensitizer, energy transfer to the reactive sites on the polymer, and the formation of crosslinks. In fact, the triplet yields of aryl naphthothiazole derivatives, a widely used class of sensitizers, are considerably higher in the more viscous polymeric matrices. These ϕ_{isc} in the polymer approach, however, a value of only ca. 0.7. As a result a search for more efficient triplet sensitizers led to a new class of compounds: 5- and 7-substituted 3-ketocoumarins.

As a model for study of the bimolecular processes in polymers, we chose exciplex and excimer probes. The following conclusions were drawn: 1. Several exciplex and excimer emissions in polymeric media are considerably shifted to shorter wavelengths as compared with the maxima measured in fluid media, indicating that interactions are impaired in polymeric matrices.

2. Emissions from the polymer matrix above the glass-transition temperature are similar in wavelength and temperature dependence thereof to those observed in fluid solutions.

3. Improper orientation of the reactants in polymers is responsible for the shift observed in excimer emission and for a part or all of the shift in exciplex emissions.

4. Little if any difference is observed between exciplex emissions in polymers of low and moderate macroscopic polarities. This may be attributed to two causes: a) Due to improper orientation the dipole moment of the exciplex in the polymer is expected to be smaller and, therefore, less solvation energy can be gained. b) The segmental motion of the polymer required to properly solvate the complex is probably too slow at room temperature compared with the lifetime of the exciplex.

5. Bichromophoric molecules, which form exciplexes in fluid media, fail to reach an exciplex configuration when dissolved in polymers.

INTRODUCTION

Photochemistry in polymer systems must be considered from two aspects, that of the polymer or polymeric host and that of added or dissolved low-molecular-weight probes or guest solutes. An arbitrary classification of various well-known photochemical processes in terms of these two aspects and relating to their behavior is as follows:

PHOTOCHEMISTRY IN POLYMER SYSTEMS

<u>Polymers</u>	<u>Guest</u>
Photodegradation	Photoinitiation (polymerization)
Photografting	Modification of Excited States
Photocrosslinking	Modification of Lifetimes
Photomechanical Effects	Steric Interference
Down Chain Energy Migration	Recombination Reactions
	Aggregation

Fig. 1. Classification of photochemical processes in polymers

One must consider all combinations of chemical and physical interactions of chromophores attached to or dissolved in polymers, interactions between more than one guest molecule of the same or different species, and macromolecule chain interactions. The type and degree of interaction determine specific effects upon each of the above components. These effects in turn can lead to control of photophysical, photochemical, or resultant ground-state chemistries.

Photoisomerization of guest molecules in polymer matrices

Gegiou, Muszkat and Fischer (1) reported that the quantum yield of photoisomerization of trans to cis stilbene decreased with increasing viscosity. Their work, originally carried out in glasses, led them to discover that in polymers as well free-volume decreases with lowering of temperature reduce the space available for rotation of the phenyl groups from trans to cis configuration. They postulated that an increase in free volume was necessary during isomerization from trans to cis stilbene.

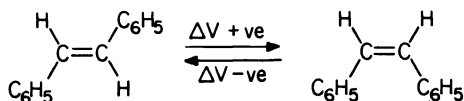


Fig. 2. Photoisomerization of stilbene in polymeric matrices

It was suggested that a polymer matrix such as polyisobutylene did not inhibit photoisomerization at temperatures above the glass-transition temperature (T_g) because above T_g sufficient free volume existed for normal solution kinetics to dominate. Many such experiments in polymer matrices have dealt with photochemical conversion of isomers followed by thermal return or equilibration. They indicate that the free volume can be a critical factor in the ability of a guest to isomerize to another form. These probes, therefore, are sensitive to the free volume, microscopic viscosity, or steric interference at particular environment which the probes sense as average values. Such investigations have all revealed that kinetic discontinuities occur during temperature descent near the glass-transition temperature. Most investigations have shown that unimolecular reactions such as isomerization of small molecules proceed via first-order kinetics above the glass-transition temperature, T_g . Below T_g , complex kinetics result and appear to be the result of a multiplicity of different first-order processes. The most appealing explanation is that a whole range of different guest sites exist. They in turn have various free-volume characteristics. This consideration results in a spectrum of microscopic viscosities, each determining a characteristic kinetic behavior which when observed as an average figure appears very complex. Others reported similar findings for a variety of probe-polymer combinations (2-6).

Effect of polymer environments on excited states

In solutions of polymers the space between polymer chains which is available for unhindered diffusion may be quite large. In this case the microscopic viscosities will not even approximate the high macroscopic viscosity and processes can occur as in dilute polymer-free solutions. The space would then be sufficient for nonassociative excited species to diffuse rapidly through the polymer network as though they were dissolved in a pure solvent. Heppel (7) reported that the translational coefficient of anthracene in solution was unaltered by

Polyisobutylene gels or solutions - no effect

Polyisobutylene films - reduced

Polyvinyl alcohol or gelatin gels - reduced
due to hydrogen bonding between polymer
chains

Fig. 3. The effect of viscosity on the translational coefficient of anthracene

the presence of polyisobutylene even when the system was concentrated to the form of a gel. The network was thus more open than that found in hydrogen-bonded systems such as glycerol, polyvinyl alcohol, or gelatin gels. However, in "dried-down" coatings the microscopic viscosity exerts effects on diffusion of molecules as small as oxygen. Buettner (8) concurred by finding similar effects in gelatin films containing 2-naphthol as guest molecule.

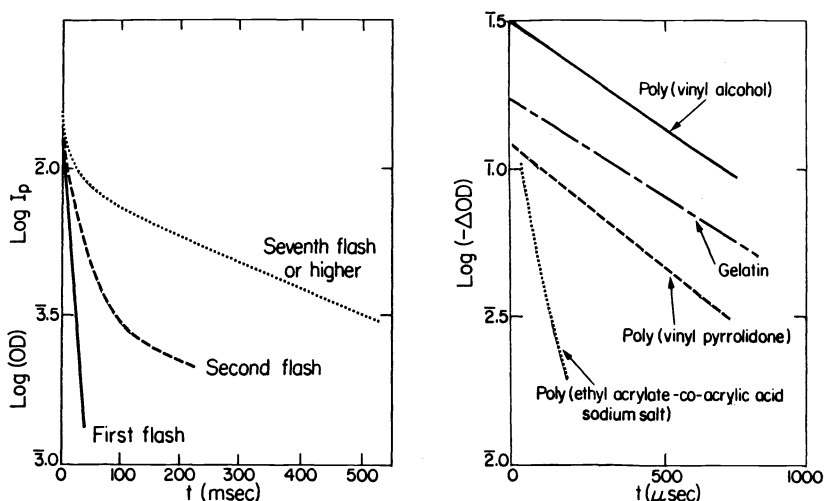


Fig. 4. Decay of the triplet state: left - of 2-naphthol in a gelatin film; right - of erythrosin in various matrices

Flash photolysis revealed that the original film, saturated with oxygen could be starved from oxygen by repeated flashing. Oxygen quenching of the triplet of 2-naphthol was very marked during the first and second flashes. After multiple flashing, oxygen quenching was strongly reduced because of the low diffusion rate of oxygen through gelatin as a result of efficient interchain hydrogen bonding. Polymeric esters such as polymethyl methacrylate have no sites for interchain association by hydrogen bonding. They, therefore, showed little impediment to the migration of oxygen in contrast to self-associating polymers such as polyvinyl alcohol and gelatin. Another consequence of the rigid medium and its reduction of the rate of diffusion was that no self-quenching of the triplet was observed for either 2-naphthol or erythrosin.

Polymer-attached chromophores

Up to this point we have discussed only the effect of media on dissolved guest molecules. If we append or incorporate a photoisomerizable chromophore onto or into a macromolecule, photoisomerization can cause dimensional changes of the polymer chains. Thus, photoinduced mechanical effects have been produced when photoisomerizable groups were incorporated into polymer backbones. Angolini and Gay (9) prepared linear polyimides having azo dyes incorporated into the backbone which were then examined as semicrystalline films. The as-prepared

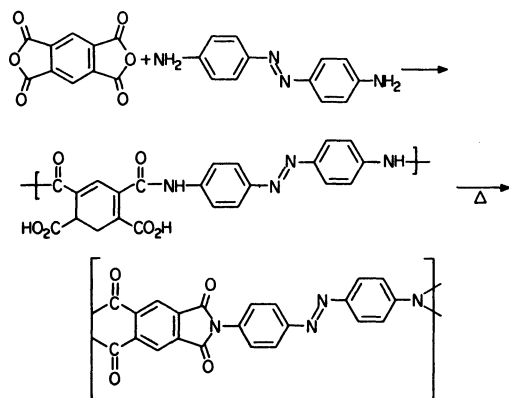


Fig. 5. Photocontractable polyimide

trans azo form when held at constant length during irradiation formed the *cis* isomer and simultaneously exhibited stress increases. Relaxation in the dark caused relief of the stress due to conversion of the *cis* to the *trans* form. Smets and DeBlauwe (10) prepared copolymers of ethyl acrylate with bis(spiropyran-acrylate) crosslinks and followed timewise the photomechanical contraction of their films under constant load. In the dark the films

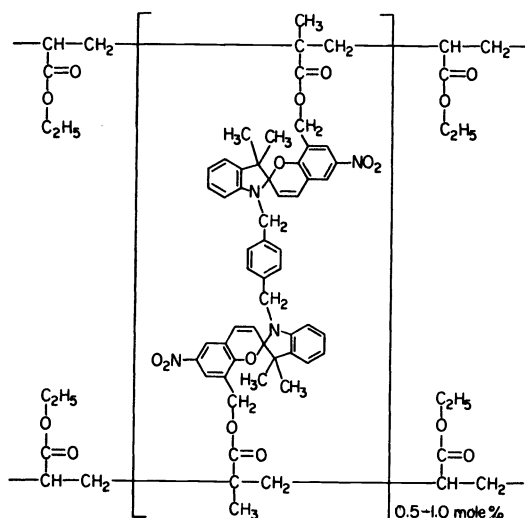


Fig. 6. Photocontractable crosslinked polyacrylate

returned to the elongated configuration. Several such cycles verified the reversibility of the system. In such systems irradiation opened the spiropyran structures to merocyanine dye moieties, which are more flexible and increase the polymer chain segment mobility. Stretch orientation of such films induced a stress which reduced the rate of decoloration or fading of the merocyanine form since the ring-forming moieties could less easily come together to form the spiropyran form. Lovrien (11) observed a photoinduced solution viscosity effect in aqueous solutions of a copolymer of acrylic acid and an acrylamidoazo dye monomer. The azo-

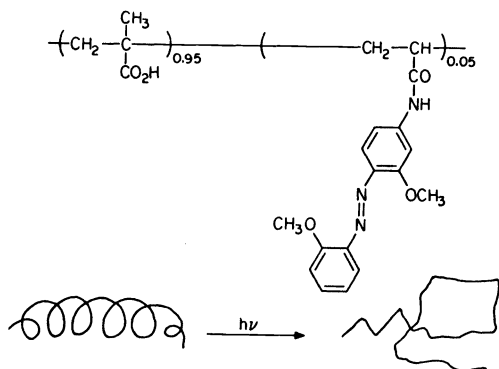


Fig. 7. Photoinduced solution viscosity change

group-bearing polymer tended to exist in the dark as hydrophobic agglomerates bearing the less polar trans form. Irradiation converted the azo group to the cis form, which exerted steric crowding along the polymer chain. The crowding effect caused extension of the polymer backbone to a more rodlike configuration and thus increased the solution viscosity. The inverse effect was found in water when the trans form of the positively charged dye chryso-phenine was associated with the negatively charged backbone of polymethacrylic acid. This produced an extended macromolecular associate. The trans form of the dye in the associate, when photoisomerized to its cis form, dissociated from the anionic backbone, allowing coiling to occur thereby decreasing the viscosity. Van der Veen and Prins (12) found that

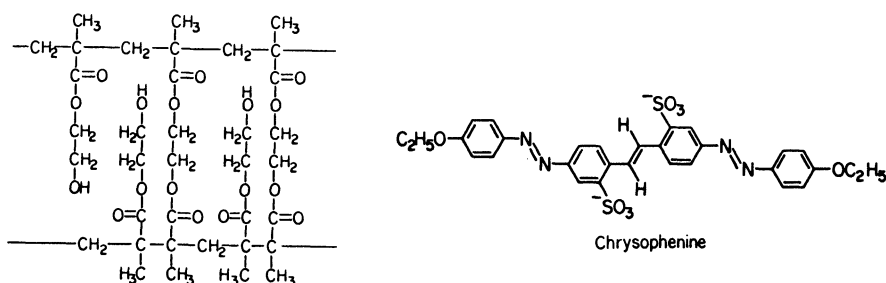
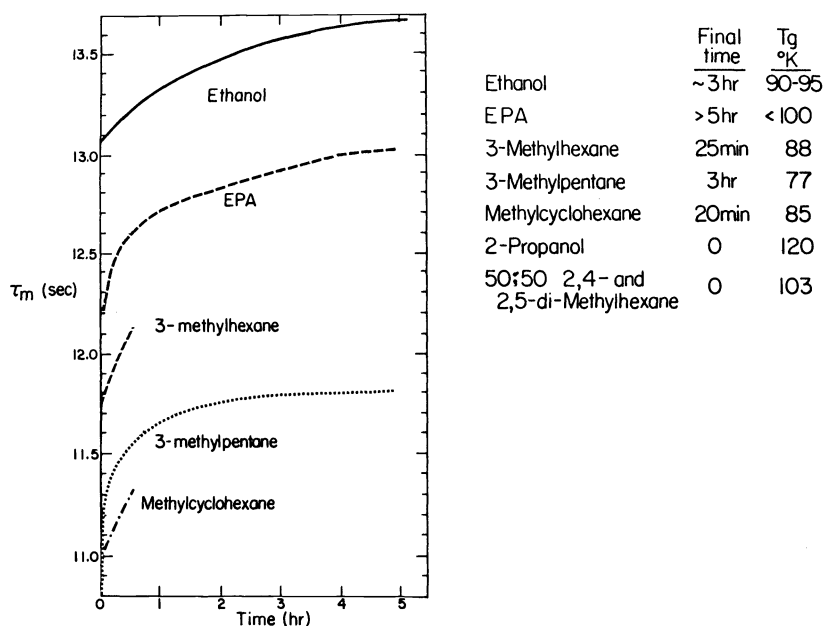


Fig. 8. Crosslinked/gel associate of chrysophenine

aqueous gel-type membranes of copolymers of 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate could be made to contract when chrysophenine thereon adsorbed was suitably irradiated and photoisomerized.

Emission of guest molecules in polymer matrices

Chromophore-bearing guest molecules in polymer matrices show phosphorescent emission at room temperature only slightly reduced from that at low temperatures. This marked difference from the temperature-related behavior of solutes in solvents indicates that the mode or modes of radiationless decay are decreased in the polymer system, since the mobility in the polymer film is limited because of the high microscopic viscosity (13). When a polymer-solute combination is cast into film by evaporation of a solvent, the solute or guest can find itself in environments which can differ greatly in terms of the local viscosity or free volume unless thermal relaxation is permitted. Similarly, Martin and Kalantar (14) found that at low temperatures (77°K) in glasses such as EPA, the triplet lifetime of benzene and related systems increased over periods of 5-6 hours. If the glasses were allowed to relax over a period of hours before the measurements were made, the terminal time-series values

Fig. 9. Phosphorescence lifetimes of C_6D_6 in glasses of 77°K vs time

resulted. Furthermore, the effect was found only in glasses whose glass transition was within 30° of 77°K. This treatment permitted thermal relaxation to occur. Thus, the configurational relaxation processes in the glass were directly related to the phosphorescing guest's triplet lifetime. Somerall, Dan and Guillet (15) sensed the molecular motions of polymers in coatings by following the change of phosphorescence intensity of pendant aromatic groups as the samples were warmed from 77°K. Discontinuities in the emission intensity signaled the onset of subgroup motion. For polystyrene and its copolymers the onset of crankshaft motion (T_g) was very well defined.

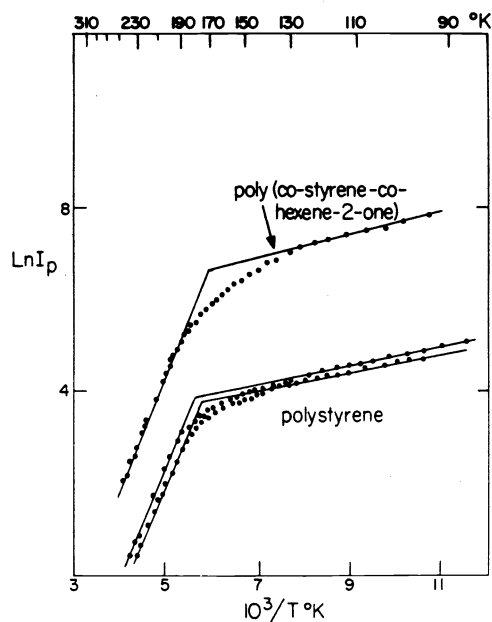


Fig. 10. Arrhenius curves for the phosphorescence of polystyrene polymers

Microenvironmental polarity effects

Other photochemical investigations, particularly in solution, have offered the opportunity to consider the microenvironmental polarity along polymer chains and at side groups many angstroms away from the main chain. During a study of mobility and solvatochromic effects of polymer chains, Vandewijer and Smets (16) found that the polarity of microscopic environments along spiropyran-bearing polymer chains could be sensed by attached merocyanine dyes. Merocyanine dyes of the type used exhibit drastic changes in their absorption spectra with changes in solvent polarity. Model dyes and the corresponding polymers showed essentially

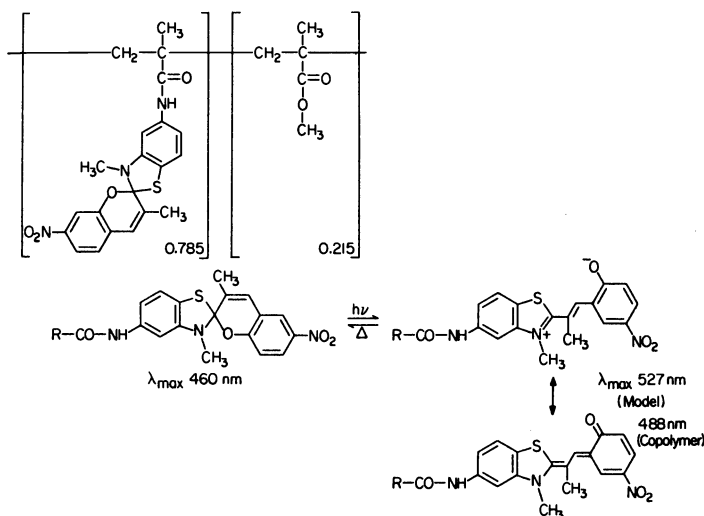


Fig. 11. Solvatochromic copolymers and model compound

the same spectra in benzyl alcohol. With somewhat more polar comonomers such as methyl methacrylate or methacrylonitrile, larger differences between the polymers and the model were found, particularly in polar solvents such as acetone, chloroform or tetrahydrofuran. An interesting effect was produced by the addition of hexane to pyridine solutions of the polymer. This nonsolvent caused the polymer chains to coil forcing the merocyanine pendant groups to lie close to the hydrocarbon backbone.

Photoisomerization of *trans*- to *cis*-nitro stilbene-type polymers was studied by Mikes, Strop and Kalal (17), who prepared copolymers of *trans*-N-4-(4'-nitrostyryl)phenyl methacryl-

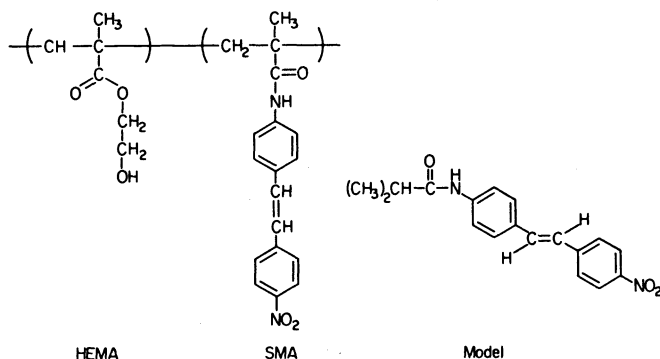


Fig. 12. Comparison of microenvironmental polarity along a chain with that found in solution

amide and 2-hydroxyethyl methacrylate (HEMA). Solutions of the copolymer and the model in either 2-ethoxyethanol or methanol were irradiated. The polymer reached its steady state faster than did the model. This was attributed to the lower microenvironmental polarity in the area of the polymer compared with that of the model with solvent. Mikes, Strop and Kalal (17) also used styrylpyridium-HEMA and vinylpyridine copolymers to show that the polarity of the chain itself caused microenvironmental polarity changes which modify the charge-transfer absorption bands. Strop (18) using a styrylpyridyl methacrylamide copolymer found that its polarity in water corresponded to that of a solution of 45% methanol in water. The HEMA copolymer when dissolved in aqueous 15% *t*-butanol showed a microenvironmental polarity corresponding to that of 45% *t*-butanol.

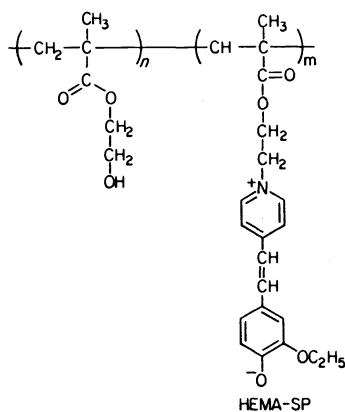
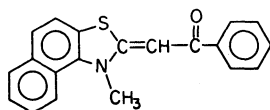


Fig. 13. Microenvironmental polarity studies using a polyionomer

PHOTOCHEMISTRY RELATED TO PHOTOCROSSLINKABLE POLYMERS

Our own interest in photochemistry related to polymers stems from efforts to improve the efficiency of photocrosslinking of and extend or control the spectral response of polymers used as photoresists and in printing plates. In an earlier report we dealt with a number of the problems involved in designing the photocrosslinkable polymers used in various imaging systems (19); we also pointed out that the broad range of structural types of compounds which function as sensitizers with photocrosslinkable polymers led us to the idea that not all classes functioned strictly via triplet energy transfer. We concluded that sensitizers such as BN were true triplet sensitizers but that hydrocarbon types such as phenanthrene suffered from competing photochemical addition reactions when ethyl cinnamate was present. Evidence



N-methyl-2-benzoyl- β -naphthothiazoline (BN)

for exciplex intermediates was put forward although exciplex emission was not found until the combination of pyrene and cinnamitrile was studied. Pyrylium salts were shown to cause the formation of low polymers with dienes and induced atypical photostationary states with stilbene. Although the ketones studied appeared to function as typical triplet sensitizers, the relationship between ϕ_{ISC} to the triplet and their ability to function in photocrosslink formation could not be correlated. This non-correlation was found when a series of BN-type sensitizers were synthesized in hopes that sensitizers having increased ϕ_{ISC} values might lead to photocrosslinking efficiencies greater than that found with BN. Table I shows that a

Table I

ϕ_{ISC} Values of Substituted BN-Type Sensitizers

ϕ_{ISC}

R / Solvent	C_6H_6	$CH_3CO_2C_2H_5$	CH_3CN
(BN)	0.24	0.15	0.033
-I	0.34	0.144	0.037
-I	0.15	0.069	0.014
(TN)	0.6	0.33	0.046
		0.375	0.082
	~ 0.57	0.19	0.018

range of ϕ_{ISC} values resulted from the structural modifications. The *p*-iodo-substituted BN had a 50% increase in ϕ_{ISC} whereas the thiophene analog showed ϕ_{ISC} increased by threefold. The values of ϕ_{ISC} in ethyl acetate were considered approximate to those expected in polyvinyl cinnamate since the polarities of the two media are quite close. However when BN and its thiophene analog TN were compared using monochromatic (405 nm) exposure with polyvinyl cinnamate as the crosslinkable polymer, the efficiencies were nearly identical. Comparison of BN with Michler's ketone using the isoabsorptive wavelength 377 nm, for irradiation, showed that BN was 70% as efficient as Michler's ketone, whose ϕ_{ISC} in solution approaches unity. It therefore seemed reasonable to us to propose that the ϕ_{ISC} values of all the BN sensitizers listed are higher in the polymer matrix and to also propose that their radiationless decay is reduced in the polymer matrix. Although the ϕ_{ISC} of these compounds is higher in polymeric matrices (0.7), it is far less than unity, indicating that the photographic response in the 400 nm range, where BN has maximum absorbance, can conceivably be increased. Furthermore, BN and its derivatives give practically no response above 460 nm. These compounds cannot, therefore, be used for exposure in the 500 nm range, for example with the visible output of the argon ion laser (488 and 515 nm). A search for efficient sensitizers for the 400 nm range (output of Hg high-pressure lamps) and for sensitizers for the 500 nm range was undertaken.

In general efficient triplet sensitizers for photocrosslinkable polymers would be required to have most of the following features:

1. High extinction coefficient ($\sim 10^4$) to ensure a considerable absorption of the incident light at a relatively low concentration of the sensitizer in the polymer matrix.
2. High efficiency of isc to the triplet state.
3. High enough triplet energy to ensure an efficient energy transfer to the photoactive chromophore of the polymer.
4. In order to extend the spectral response of the polymer to the longest possible wavelength, a sensitizer with a very small singlet-triplet gap would be required.
5. The sensitizer must have other nonphotochemical properties, e.g., high enough solubility in the coating solvent and in the polymer.

Ketones, particularly diaryl ketones, such as benzophenone, are known to have relatively high triplet yields. High extinction coefficient would require the possession of a $\pi-\pi^*$

or CT transition in the desired spectral region as, e.g., with Michler's ketone. Certain derivatives of 3-ketocoumarins with electron-donating substituents mainly in the 7-position fulfilled most of these requirements and are very promising triplet sensitizers not only for polymers but also for solution reactions.

Table II

Structure and Spectral Characteristics of Ketocoumarins

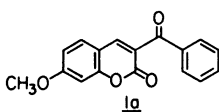
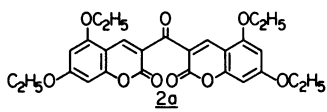
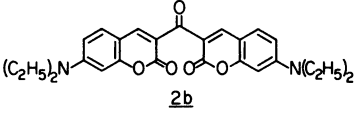
Structure 1			Structure 2		
R	λ_{\max} (nm)	ϵ ($\times 10^3$)	R	λ_{\max} (nm)	ϵ ($\times 10^3$)
(5)7-alkoxy group	350-380	17-21	(5),7-alkoxy group	380-390	~46
7-dialkylamino	410-430	35-39	7-dialkylamino ^(a)	450-470	60-90

R₁: phenyl, pyridyl, thienyl, furyl, etc. (a) including open chain derivatives cyclic and fused-ring

Compounds 1a, 2a and 2b are selected examples of efficient sensitizers of this class of compounds covering a good range of the near-UV and the visible region.

Table III

Intersystem Crossing Quantum Yields and Triplet Energies of Ketocoumarins

Structure	λ_{\max} (nm) ^(a)	ϵ ^(a)	Φ_{isc} ^(b)	E_T ^(c)
	345	19,000	>0.9	ca.59
	398	46,000	~1.0	ca.56
	450	92,000	0.94	ca.52

(a) in C₆H₆
 (b) in C₆H₆ using stilbene isomerization technique
 (c) in EPA (77°K), from the emission spectrum (tangent at the short wavelength region) values in kcal/mole

It should be noted that the absorption spectra of these compounds, as for most other sensitizers, are shifted to longer wavelength in polymeric matrices. Compound 2b has λ_{\max} of 464 nm in diphenylcyclopropane carboxylate ester of polyvinyl alcohol (DPC) (20) and still has strong absorption in the polymer at 488, the argon-ion laser line. A feasible system using 2b and DPC for argon ion laser exposure was achieved.

Compound 2a is most useful for Hg high-pressure exposure. With such a light source 2a is 1.6 times more efficient than BN, a figure reflecting the increase in ISC efficiency from 0.7 or slightly less for BN to almost unity for 2a. Both compounds show similar absorption maxima and extinction coefficients as well as triplet energies. Compound 1a can be used where almost colorless materials are desired.

The fact that the relative ISC efficiencies measured in solution of BN and TN failed to correlate with these practical performances in polymers led us to consider more closely the role of the polymer matrix. Interaction of excited states with the matrix could reduce deactivation and thus eliminate that pathway, making sensitizers such as BN and TN equal in efficiency.

Most of the photochemical information used to design an optimum light-sensitive system comes from solution studies. The question is how does the rigidity of a polymeric matrix affect the course of any of the photochemical steps involved in the process. In other words, how reliable is it to extrapolate from solution photochemistry to photochemistry in a polymeric matrix? Several steps intervene between the excitation and the formation of a

crosslink in triplet-sensitized photocrosslinkable systems such as shown schematically in Fig. 14.

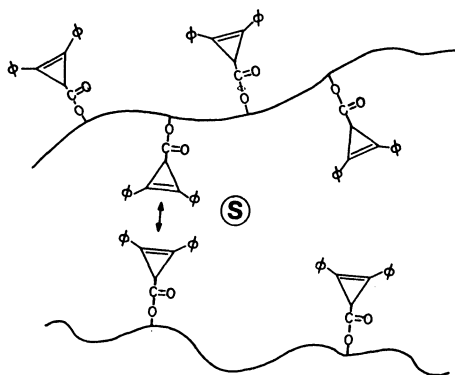


Fig.14. Schematic diagram of a triplet-sensitized photocrosslinkable system

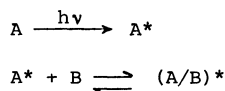
These steps are:

1. Intersystem crossing to the triplet: $^1S^* \xrightarrow{\text{isc}} ^3S^*$.
2. $^3S^* + \text{polymer chromophore} \longrightarrow S + ^3\text{polymer chromophore}^*$
3. $^3\text{polymer chromophore}^* + \text{polymer chromophore} \longrightarrow \text{crosslink}$

Exciplexes in fluid and rigid media

The rigidity of the medium can affect the photochemical reactions at any of these steps. Steps 2 and 3 deal with bimolecular interactions occurring on a relatively short time scale. To investigate the effect of the rigidity of the medium on short-lived bimolecular interactions we chose exciplex emissions as a probe.

Exciplexes are complexes in the excited state, which do not have binding interaction in the ground state:



The energy profile of an exciplex is given in Figure 15. The photophysics of exciplexes in solution has been intensively investigated since the discovery of the phenomenon over a decade ago (21). The exciplex emission is characterized by being broad, structureless (due to decay to a repulsive ground-state) and red-shifted relative to the corresponding monomeric fluorescence. The exciplex emission is also characterized by a strong dependence on the medium polarity.

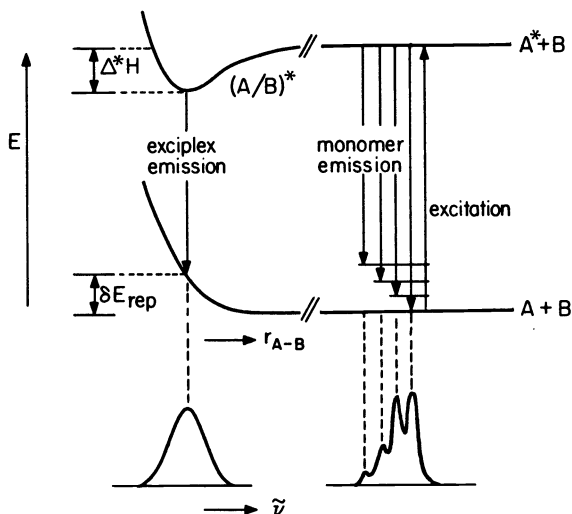


Fig. 15. An energy diagram of an exciplex, after A. Weller, *Z. f. Phys. Chem.*, **69**, 183 (1970).

The intensity of the exciplex emission is usually, but not invariably, strongest in nonpolar solvents. Increasing the medium polarity leads to decrease of the intensity and further shift of the exciplex band to the red. To study the effect of medium rigidity on such processes it is, therefore, necessary to compare data in media of very similar polarities.

The anthracene (3)/*N,N*-dialkylaniline system is one of the most extensively studied examples of radiative exciplexes (22). In the present study, we used 4 in order to have a better analog of the chromophore chemically bonded to the polymer.

Comparison was made of the three related systems given in Table IV, namely of 3 and 4 dissolved in toluene and in polystyrene as well as 3 dissolved in a 20:1 copolymer of styrene and 4-(*N,N*-dimethylamino)styrene (5) (23).

Table IV

Wavelength Maxima of the Exciplex Anthracene Dimethyltoluidine in Fluid and Polymeric Media

Fluorescing Compound	Exciplex Electron-Donor Component and Medium	λ_{\max} of Exciplex Emission (at +30°C) [nm]
	+ in	515
	+ in	490
	in	480

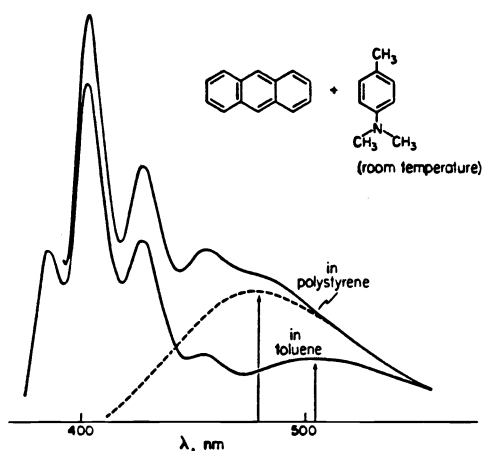


Fig. 16. Emission spectra (uncorrected) of anthracene (3) in the presence of *N,N*-dimethyl-*p*-toluidine (4) in toluene and in polystyrene.

The Stern-Volmer slope of the fluorescence quenching of (3) by (4) in aerated toluene at room temperature is 47 l/mol. In polystyrene coatings, the corresponding Stern-Volmer slope is much lower (1.4 kg/mol) as expected from the highly decreased rate of quencher diffusion.

At room temperature, the maximum of the exciplex band in toluene is at 515 nm, whereas in the polystyrene film this band is shifted by 25 nm to shorter wavelengths (Fig. 16). When the dimethylaniline moiety is attached to the polymer chain (5), the exciplex band is further shifted by 10 nm to shorter wavelengths.

Temperature effect on exciplex emission

Moreover, the maxima of the exciplex emission in all cases are temperature dependent. The maxima in toluene shifts to shorter wavelengths with increasing temperature. Similar data have been reported by Itoh (24) for a different exciplex in hydrocarbon solvents. The emission in polystyrene, however, is shifted to longer wavelengths with increasing temperature. A value similar to that observed in the fluid medium is obtained in the polymeric matrix when the measurement temperature approaches the glass-transition temperature (T_g) of

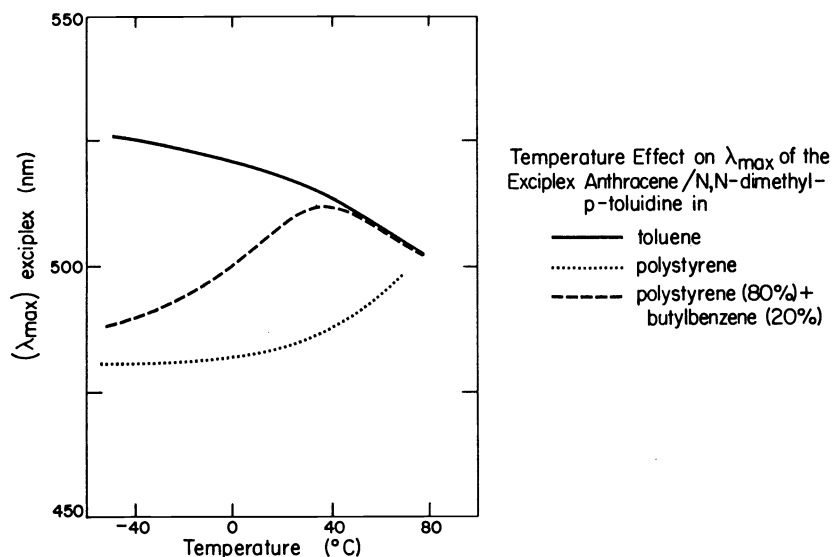


Fig. 17. Temperature effect on λ_{\max} of the exciplex anthracene/N,N-dimethyl-p-toluidine

polystyrene. This point is more evident when 20 wt % of *n*-butylbenzene is included in the polystyrene matrix in order to lower the glass-transition temperature. The maximum of the exciplex in this mixture follows the same pattern as in pure polystyrene by shifting to longer wavelengths with increasing temperature and finally reaches the value measured in toluene at temperatures close to the T_g of the *n*-butylbenzene-polystyrene matrix. Further increase in the temperature of the mixed medium leads to a shift to shorter wavelengths, similar to that measured in toluene.

It is known that the dielectric constant (ϵ) of fluids increases with decreasing temperature. This, however, cannot account for the changes in exciplex emission in toluene. At +30°, *o*- and *p*-xylene have dielectric constants very similar to those of toluene at -40° and +80°, respectively, which are the lowest and highest temperatures used in the present measurements (Table V). The exciplex emission maxima in all three solvents at 30° vary only

Table V

SHIFT OF THE EXCIPLEX MAXIMA IN TOLUENE AND XYLENES

Toluene		at +30°C	
Temp. (°C)	ϵ	Solvent	ϵ
-40	2.542	<i>o</i> -xylene	2.541
+30	2.365	toluene	2.365
+80	2.244	<i>p</i> -xylene	2.254
$(\Delta \lambda)^{\text{exc.}} = 25 \text{ nm}$		$(\Delta \lambda)^{\text{exc.}} = 3 \text{ nm}$	
-40° → +80°		<i>o</i> -xylene → <i>p</i> -xylene	

by 2-3 nm, whereas the shift due to temperature change in toluene is 25 nm. Moreover, a temperature-dependent shift of λ_{\max} similar in magnitude to that measured in toluene was observed in *n*-octane, which has a smaller temperature coefficient for the dielectric constant variation, is nonaromatic, and is one of the least polar solvents. We also observed a

similar change in the exciplex maxima with temperature for the intensively investigated anthracene/dimethylaniline in methylcyclohexane.

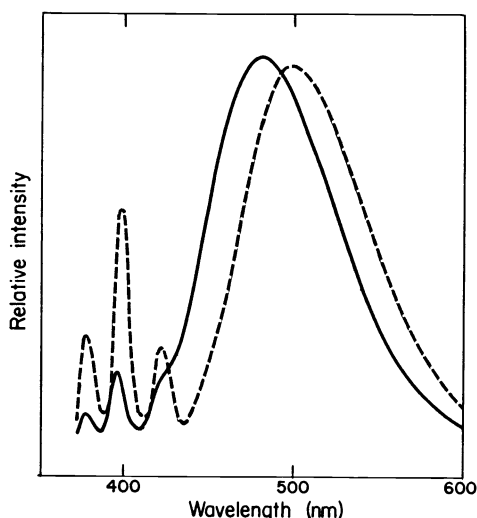


Fig. 18. Corrected emission spectra of $\frac{3}{4}$ exciplex in *n*-octane: at +50° and at -40°.

It can be speculated that the change in wavelength maximum of the exciplex with temperature in a fluid medium or in polymers above T_g may be due to a change in the energy profile of the

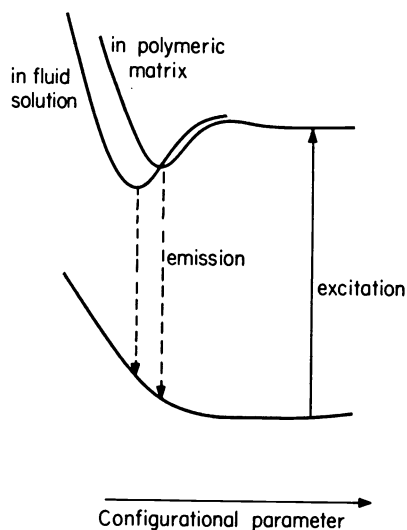


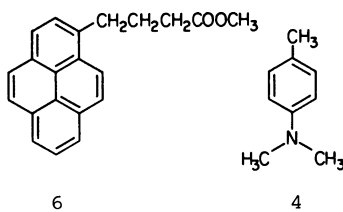
Fig. 19. Hypothetical profiles of an exciplex in fluid and rigid matrices

exciplex. It is conceivable that the depth of the energy minimum and/or the average distance between the components might vary with temperature. The shifts to shorter wavelength with decreasing temperature in polymeric matrices at temperatures below T_g could be due to improper orientation and/or larger separation of the exciplex components as compared with those in fluid media. These findings support the proposal that interactions occurring on the sub-microsecond scale are not as favorable in polymers below the T_g as they are in solution. This impaired access of an excited molecule to others in a polymeric matrix may contribute to the occasional deviation between solution and polymer photochemical reactivity.

Comparison of effect of medium rigidity on excimers and exciplexes

To explore the origin of the decreased stability of exciplexes in polymers, compounds capable of forming both exciplexes and excimers are required for comparison, as shown below. Pyrene and many of its derivatives form excimers efficiently, and in the presence of electron donors or acceptors emitting exciplexes are formed (26-28). Pyrene also has a much longer lifetime in the singlet excited state (28) (300-500 nsec) than anthracene (29) (~5 nsec), which was used in the above study. It is of interest to find out whether such a dramatic

increase in the lifetime could allow for the formation of exciplexes with more optimum orientation in the polymers. In the following investigation methyl 4(1-pyrenyl)butyrate (6) was used because it has a much greater range of solubilities than pyrene itself.



The exciplex of 6 and 4 emits at a λ_{\max} of 495 nm in toluene at room temperature. The corresponding emission in polystyrene occurs at a λ_{\max} of 460-465 nm. The difference in wavelength of the exciplex emission maxima ($\Delta\lambda = 30-35$ nm) for 6/4 in fluid and polymer is slightly larger than that obtained for anthracene/4 (25 nm). This indicates the increase in the lifetime of the excited molecule by almost two orders of magnitude does not lead to the formation of a more stable exciplex in the polymeric matrix. The slight increase in $\Delta\lambda$ between the exciplex of 6 and that of anthracene may be attributed to the larger size of the pyrene derivative with the consequent decrease in mobility.

The λ_{\max} of the exciplex emission of 6/4 in polystyrene also varies with temperature in the same way as seen previously for the anthracene exciplex. At higher temperatures, as the polymer becomes more fluid, the emission occurs at longer wavelengths and above T_g of the polymer the emission approaches that in fluid solution. This phenomenon is clearly demonstrated in low-molecular-weight polystyrene, which has a lower T_g (54°C) than that of high-molecular-weight polystyrene (105°C). The low-molecular-weight polystyrene film behaves as a fluid at approximately 30°C lower temperature than does the high-molecular-weight polystyrene at a given concentration of exciplex-forming solutes. The increased mobility of the polymer allows the formation of a more stabilized exciplex. These experiments, however, give no information on whether the destabilization below T_g occurs because of a less favorable orientation for the exciplex components or because the polymer is less able to solvate the exciplex.

The orientation and the solvation effects can be differentiated using a comparative study on excimer emissions. Since excimers have negligible dipole moments, their emission spectra are independent of the solvent polarizability (28). The excimer of 6 was studied in three fluid/polymer pairs: toluene/polystyrene (PSt), methyl isobutyrate/polymethyl methacrylate (PMMA), and methyl benzoate/polyvinyl benzoate (PVB). These systems were chosen to have similar polarities within each pair but to give a range of polarities among the three pairs.

The maxima of the excimer emission of 6 in all three fluid solutions are similar, as expected (Table VI). In the polymer films the corresponding maxima are also similar but are shifted by about 40 nm from those in fluid solutions. This shift is unambiguously due to improper orientation of the monomer components of the excimer in the polymer matrix, since solvation does not play any significant role in excimer emission. Accordingly, most, if not all, of the shift between exciplex emissions in PSt and toluene should be the result of destabilization of the complex caused by improper orientation in the polymeric matrix. As with exciplexes, the excimer emission in polymer films approaches that of the fluid medium when the temperature is raised (Table VII).

TABLE VI. Excimer maxima (nm) of compound 6 in different fluid and polymeric media

Fluid Medium	λ_{\max}	Polymeric Medium	λ_{\max}	$\Delta\lambda_{\max}$
Toluene	480	PSt	445	35
Methyl isobutyrate	480	PMMA	440	40
Methyl benzoate	485	PVB	440	45

TABLE VII. Temperature effect on λ_{\max} (+2 nm) of the excimer emission of 6 in different media

Temp.	Toluene	Low-Molecular-Weight PSt	High-Molecular-Weight PSt
25°	480	465	450
75°	473	473	463

Comparison of the excimer data with data for exciplexes in moderately polar media should reveal the role of solvation in such polymer matrices. The exciplexes of anthracene and of the pyrene derivative 6 with dimethyltoluidine (4) were measured in the three solvent/polymer pairs mentioned above. The data are given in Tables VIII and IX, respectively.

TABLE VIII. Exciplex maxima (nm) of anthracene/dimethyltoluidine in different fluid and polymeric media

Fluid Medium	λ_{\max}	Polymeric Medium	λ_{\max}	$\Delta\lambda_{\max}$
Toluene	515	PSt	490	25
Methyl isobutyrate	550	PMMA	500	50
Methyl benzoate	560	PVB	503	53

TABLE IX. Exciplex maxima (nm) of methyl 4-(1-pyrenyl)butyrate with dimethyltoluidine in different fluid and polymeric media

Fluid Medium	λ_{\max}	Polymeric Medium	λ_{\max}	$\Delta\lambda_{\max}$
Toluene	495	PSt	460-465	30-35
Methyl isobutyrate	520	PMMA	460-465	55-60
Methyl benzoate	530	PVB	465-470	60-65

From the data in Tables VIII and IX, it is evident that the exciplex emissions in fluid media are, as expected (30), strongly dependent on the polarity, or more correctly on the polarizability of the solvent. On the other hand, the exciplex emissions in the different polymers are very similar. As a result, the shift between exciplex emission in rigid and fluid media, $\Delta\lambda$, almost doubles on going from the low-polarity media (toluene/PSt) to those of moderate polarities (methyl isobutyrate/PMMA and methyl benzoate/PVB).

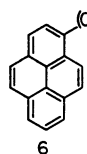
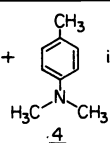
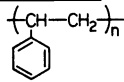
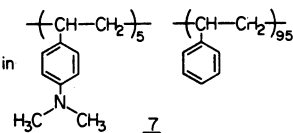
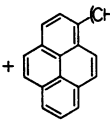
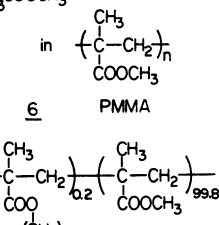
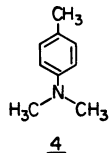
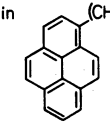
This insensitivity of the exciplex maxima to the polarity of the polymer can be attributed to two reasons: a) As a result of improper orientation in the polymer, the dipole moment of the exciplex is expected to be smaller, which would lead to less solvent dependency of the emission. b) The segmental motions of the polymers required to solvate properly the complex are probably too slow at room temperature compared with the lifetime of the exciplex (~ 100 nsec).

It is the combined effect of this poor solvation and the restricted orientation in polymers of moderate polarities such as PMMA and PVB which causes a short-wavelength shift in λ_{\max} of the exciplex of 50-60 nm as compared to those in fluid media of comparable polarities.

Exciplex components attached to polymers

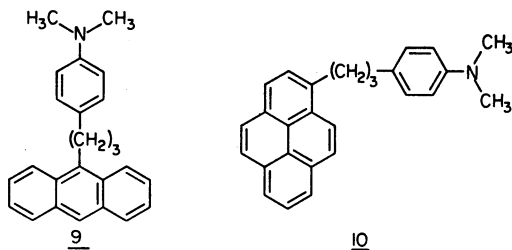
In the experiments mentioned above, the exciplex components were simply dissolved in the polymer film. In the following experiments, systems in which one of the reactants was attached to the polymer were investigated. The copolymers 7 and 8 were used in this study. As shown in Table X, the exciplex emission obtained from 6 dissolved in 7 is very similar to that from 6 and 4 dissolved in PSt, and the exciplex from 4 dissolved in 8 is very similar to that from 6 and 4 dissolved in PMMA. This indicates that attachment of either component of the exciplex to the polymer does not further reduce the degree of interaction with the dissolved component as compared with systems where both reactants are simply dissolved in the polymer.

Table X
Wavelength Maxima of Exciplexes from Derivatives of Pyrene
and Dimethylaniline

Exciplex Components and Media		λ_{max} of Exciplex (± 3 nm)
 6	+  4	463
	in  PS†	
6	in  7	465
	+  6	463
in  PMMA		
 4	in  8	460

Intramolecular exciplexes

From solution studies it is known that certain bichromophoric molecules, with the two components of an exciplex chemically attached (e.g., through a methylene chain), give strong exciplex emission (31-38). It was of interest to explore the effect of medium rigidity on such complexes. Compounds 9 and 10, which have been studied in fluid media (32,33), were used in this study.



The emission spectra of these compounds in toluene are given in Figures 20 and 21. The higher ratio of exciplex: monomer emission in 10 as compared to that of 9 is due to the longer lifetime of the singlet-excited pyrene moiety. Surprisingly, neither of these bichromophoric molecules showed exciplex emissions in PST (Figs. 20 and 21). This is an unexpected result since the local concentration of the aniline moiety at the site of the excited aromatic hydrocarbon is very high. This lack of exciplex formation indicates that the time required for the folding of the molecule to bring the two chromophores closer to each other is too long compared with the excited-state lifetime.

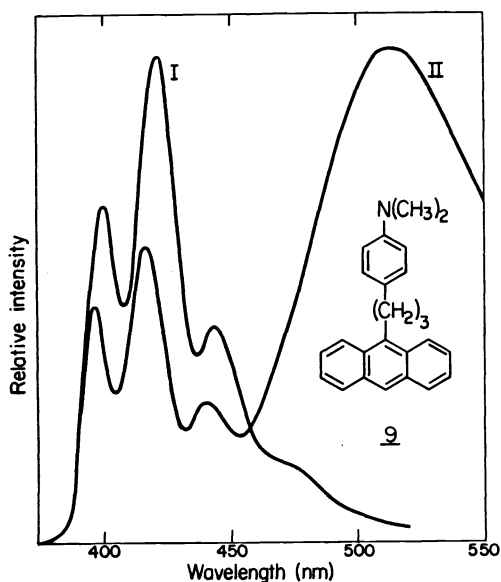


Fig. 20. Fluorescence spectra of compound **9** in polystyrene (I) and toluene (II).

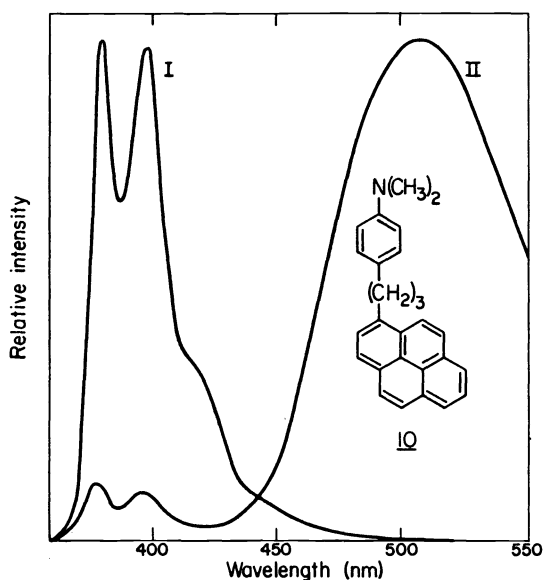


Fig. 21. Fluorescence spectra of compound **10** in polystyrene (I) and toluene (II).

An estimation of the decrease in the rate of rotation along the methylene chain in such compounds when dissolved in polymers can be made on the following basis. Since the exciplex intensity from **9** in toluene is comparable to that of the residual monomer fluorescence, one would conclude that the time required for the rotational processes to give the exciplex configuration is similar in magnitude to the lifetime of the excited hydrocarbon. The lifetime of singlet-excited anthracene is approximately 5 nsec. Therefore, the frequency with which such a molecule folds is in the order of $2 \times 10^8 \text{ sec}^{-1}$. It is reasonable to assume that the frequencies of the rotational processes in **10** are similar to those in **9**. The lifetime of singlet-excited pyrene, however, is almost two orders of magnitude longer than that of anthracene, hence the considerable increase in exciplex:monomer emission in **10**. Since practically no exciplex emission is observed from compound **10** in PSt, it can be concluded that the folding process is slower than 10^6 sec^{-1} . This means that the rotational processes required to reach the exciplex configuration are at least two orders of magnitude slower in the polymer matrix than that in the fluid medium.

In conclusion it can be stated that in polymeric matrices below T_g , bimolecular interactions on short time scale are weaker than those in fluid media. This is due to improper orientation and to poorer solvation in the polymer. At temperatures above T_g the interactions in polymers are similar to those in fluid media. The decreased interaction in polymers applies for exciplexes as well as for excimers. It does not seem to depend on the lifetime of the fluorescer between 5 and 300 nsec, and is similar in magnitude when both reactants are dissolved in the polymer or with one of them being attached to the polymer. Bichromophoric compounds connected through a methylene chain, which readily fold in the excited state in fluid media to form exciplexes, fail to do so in polymers. The rate of rotation along the methylene chain is at least two orders of magnitude slower in the polymer matrix (less than 10^6 sec^{-1} vs 10^8 sec^{-1} in fluid media).

Effect of polymer coiling on bichromophoric interactions

Our interest in controlling the deactivation pathways of excited chromophores prompted us to study the effect of coiling of macromolecules in such a way that chromophore interactions might be increased. To this end we synthesized a pyrene-bearing polyionomer of the structure shown in Fig. 22.

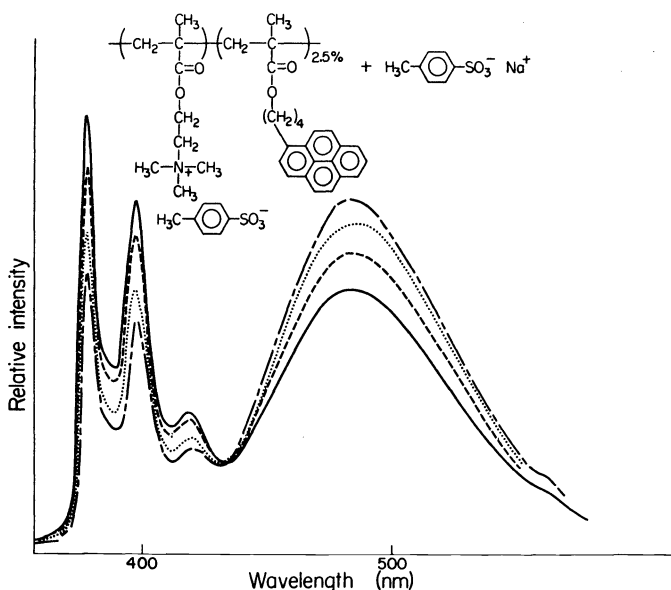


Fig. 22. Structure and emission spectra of a pyrene-bearing polyionomer in aqueous solution, —: in aqueous sodium *p*-toluenesulfonate solutions, ---, 2×10^{-4} mole/l; 7.5×10^{-3} mole/l and -.-.- 2.5×10^{-2} mole/l.

It is well established that polyionomers exist in aqueous solution in the form of extended rodlike configurations. Addition of excess counterion causes coiling of the polymer backbone to form globular structures. In agreement with this concept, the excimers to monomer ratio (E/M) increases proportionately to increase of the concentration of the added sodium *p*-toluene sulfonate. The increase in value of E/M indicates that the microscopic concentration of pyrene units is increased. A number of other pyrene-bearing polyionomers synthesized show the same effect in aqueous media.

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