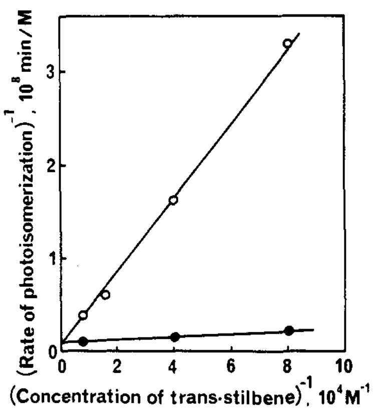

Figure 6. Dependence of the rates of photoisomerization of *trans*-stilbene to the cis form sensitized by (○) poly(phenyl vinyl ketone) and (●) phenyl vinyl ketone–2-vinylnaphthalene copolymer (content of 2-vinylnaphthalene is 16 mol %) in benzene at 10° on the initial concentration of *trans*-stilbene. The concentrations of the two polymers (~5×10^{-4} *M*) are adjusted so as to have the same absorption at 366 nm.

sumed to be close to diffusion rate constants in both cases. Therefore, the increase in the efficiency observed in these two polymer photosensitizers results from the difference in the process of (4) and (5). k_4 and k_5 are estimated to be 8×10^6 sec^{-1} and 3×10^5 sec^{-1}, respectively, assuming the diffusion rate constant of 8.5×10^9 M^{-1} sec^{-1}.[11] The relative yields of the sensitized isomerization of *trans*-stilbene by poly(phenyl vinyl ketone) and the copolymer are also estimated to be 0.01 and 0.2, respectively, for the initial concentration of *trans*-stilbene of 1.25×10^{-5} *M*. The sensitizing efficiency of the copolymer is an order of magnitude higher than that of poly(phenyl vinyl ketone) or the corresponding monomeric ketone at the low concentration regions of the energy acceptors.

Acknowledgment. The authors express their thanks to Dr. M. Simic, Hahn-Meitner-Institute, Berlin, for kindly reading the manuscript.

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Poly(2-vinylfluorenone). III. Photophysical and Photochemical Properties

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ABSTRACT: The absorption and emission spectra of poly(2-vinylfluorenone) are reported. The lowest lying excited electronic states for poly(2-vinylfluorenone) have been tentatively assigned as $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ in nature. The polymer exhibits both normal and excimer fluorescence when excited in the lowest $^1(\pi,\pi^*)$ state and in higher singlet states. No phosphorescence has been observed for dilute solutions or for thin films of poly(2-vinylfluorenone) when excited in the lowest $^1(\pi,\pi^*)$ state. Attempts to populate the triplet state in the polymer via energy transfer from 2,3-butanedione result in quenching of the donor emission but no phosphorescence or delayed emission from the fluorenone polymer. Phosphorescent emissions from photoproducts have been detected when poly(2-vinylfluorenone) is excited to higher excited states and chemistry occurring from a higher lying $^3(n,\pi^*)$ state is presumed to be responsible.

Fluorenone has been the subject of a number of studies because of its unusual spectroscopic properties, and because of its use as a triplet state sensitizer. Kuboyama has reassigned the lowest singlet–singlet transition in fluorenone as π–π^* on the basis of substituent effects.[1] Kearns[2] et al. have shown that the lowest singlet and triplet states are (π,π^*) in nature, and further showed the emission to be fluorescence. A number of workers have reported phosphorescence from fluorenone, but in general their experiments have not been conclusive, and it is likely that true phosphorescence has not been observed.[3-6] Solvent effects on the quantum efficiency of fluorenone fluorescence have been reported by Singer.[7] He suggested that the polarity of the medium can result in a reordering of the lower lying singlet and triplet states, thereby affecting intersystem crossing and fluorescence efficiencies.

Radiationless transitions in fluorenone have been discussed by Hunter,[8] and he classifies fluorenone as behaving like an extreme case for substituted ketones. He suggests in molecules such as fluorenone, in which the $^3(\pi,\pi^*)$ state is depressed far below the (n,π^*) states, degradations from $^3(\pi,\pi^*)$ should appear similar to those for aromatic hydrocarbons. Recently, Marchetti[9] has assigned the $^1(\pi,\pi^*)$ 0–0 band, and estimated the level of the $^1(n,\pi^*)$ state for fluorenone.

The availability of polymers having attached fluorenone chromophores[10] has prompted our investigations of the nature of the low lying excited states and the radiative and

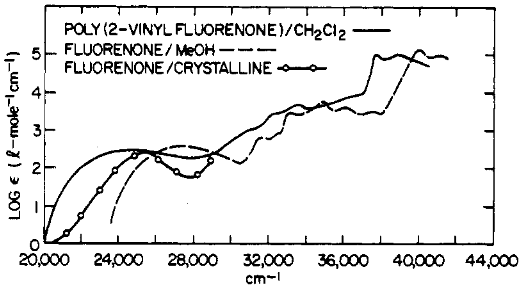

Figure 1. Electronic absorption spectra of poly(2-vinylfluorenone) in CH_2Cl_2 (—), fluorenone in CH_3OH (---), and crystalline fluorenone (O) are presented as log molar extinction coefficient against energy in wave numbers.

photochemical processes in this new vinyl polymer. These phenomena are becoming increasingly important in the understanding and control of the photodegradation and photostabilization of polymeric materials.

Experimental Section

Poly(2-vinylfluorenone). The synthesis and polymerization of 2-vinylfluorenone has been described.[10] 2-Vinylfluorenone can be readily polymerized and copolymerized by free-radical techniques to yield high molecular weight, soluble, linear polymers. The polymer investigated in this study had $\bar{M}_n \sim 300,000$ and $\bar{M}_w/\bar{M}_n \sim 6$, as determined by GPC analysis and membrane osmometry.

Emission Measurements. Fluorescence and phosphorescence spectra were obtained with a specially constructed fluorophosphorimeter. Excitation was provided by a 500 W xenon lamp and a Jarrell-Ash Ebert 0.25 m grating emission monochromator.

For 77°K spectra, optical quartz dewars were used. Phosphorescence spectra were obtained using a rotating two-window can and a McPherson Model 218, 0.3 m, grating analyzing monochromator. Fluorescence spectra were taken without the rotating can. The intensity of the dispersed emitted light was measured with an RCA 7265 end-on photomultiplier tube in a cooled (−78°) housing.

All emission spectra are uncorrected for monochromator and photomultiplier tube response. Film samples were front-surface illuminated, and all emissions were observed at right angles to the exciting light.

Phosphorescence lifetimes were obtained using the rotating can, by following the logarithmic decay on a Tektronix 564B storage scope. For some experiments, the wavelength and emission intensity data were recorded directly on magnetic tape using a Datos 9158 Spectrophotometer interface and Datos 305 data coupler (Data Graphics Corporation) in conjunction with a Texas Instruments "Silent 733" ASR data terminal. Data obtained in this way were analyzed by a curve fitting technique using an XDS Sigma 9 computer.

Results and Discussion

The absorption spectrum for poly(2-vinylfluorenone) (P2VF) and for comparison the absorption spectrum of fluorenone are shown in Figure 1. The spectra for P2VF and fluorenone are similar with the spectrum for P2VF being red shifted about 2500 cm^{-1} from fluorenone in solution and 1000 cm^{-1} red shifted from crystalline fluorenone. This shift is consistent with the experimental results reported by Kuboyama,[1] who noted that substitution at the 2 position in fluorenone produced red shifts in the long wavelength absorption band. Kuboyama was able to account for this substituent effect on the basis of simple molecular orbital theory.

The lowest singlet–singlet transition in fluorenone has been assigned as a π–π^* transition.[1] Marchetti[9] has assigned the π–π^* 0–0 band at 21,508 cm^{-1}, and he estimated the 0–0 band for the slightly higher energy n–π^* transition at 22,000 cm^{-1}. Based upon the photochemical and photophysical properties of this polymer, we believe the lowest singlet–singlet transition in P2VF remains a π–π^* transition.

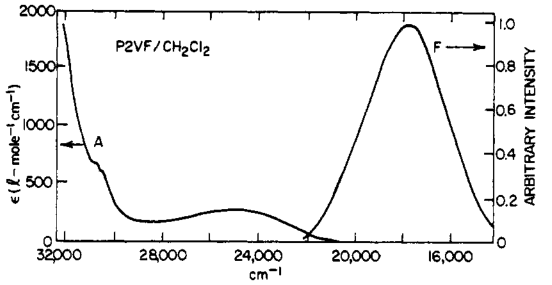

Figure 2. The electronic absorption spectrum of poly(2-vinylfluorenone) 10^{-3} M in CH_2Cl_2 is presented as molar extinction coefficient versus energy in wave numbers. An emission spectrum of poly(2-vinylfluorenone) 10^{-4} M in degased CH_2Cl_2 (high vacuum freeze–thaw method) is drawn as intensity (arbitrary units) against wave numbers.

Emission Properties. The room temperature fluorescence emission of P2VF (10^{-4} M in CH_2Cl_2) and the absorption spectrum (10^{-3} M in CH_2Cl_2) are shown in Figure 2. The emission envelope is presented in arbitrary intensity units. The fluorescence results from excitation at 405 nm, the maximum of the long wavelength absorption band. Excitation at 325 nm yields a similar emission spectrum. Fluorescence excitation (F.E.) spectra obtained by monitoring the emission intensity at 550 nm yields an absorption spectrum identical with that obtained on a recording spectrophotometer, proving that the emission observed does not originate from impurities.

The emission envelope does not exhibit good vibronic envelope inversion (mirror-image symmetry) with respect to the long wavelength absorption. This is to be expected for materials having nearly degenerate $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states.[9] There is, however, an additional factor present in the emission of vinyl polymers not present in dilute solutions of the model compounds. Aromatic homopolymers and copolymers usually exhibit anomalous long wavelength emissions commonly referred to as excimer emission. This arises from an excited state complex formed between an excited side group chromophore on the polymer backbone with a ground state chromophore, on the same or on a different polymer chain. Excimer emissions are characterized by a broad structureless emission envelope, about 4500 cm^{-1} to the red of the 0–0 band for the molecular emission.

The emission spectra for a 10^{-4} M solution of PVF in a 1:1:1 mixture of DMF, THF, and MeTHF at 298 and 77°K are shown in Figure 3. The room temperature spectrum is identical with that in CH_2Cl_2 shown in Figure 2 with a maximum around 18,200 cm^{-1}. The emission at 77°K is quite different with maxima appearing at 20,700, 19,400, and 18,400 cm^{-1}. This is more closely mirror image symmetrical with the long wavelength absorption bands in the polymer (at 22,620, 24,330, and 22,620 cm^{-1}) and has been assigned as molecular fluorescence. A difference spectrum was obtained by normalizing the intensities of the 298 and 77°K emissions at 21,500 cm^{-1} (0–0 band). This is shown in Figure 3 as a broad structureless band with a maximum around 17,000 cm^{-1}. This is characteristic of an excimer emission. Similar results have been reported for other vinyl polymers, e.g., poly(N-vinylcarbazole),[11] polystyrene,[12] and poly(1-vinylnaphthalene).[13]

The emission spectrum of a thin P2VF film (3 μm) excited at 405 nm at 298°K is shown in Figure 4. It is very similar to the room-temperature solution spectrum and it is difficult to determine the molecular–excimer contributions. Frank and Harrah have shown[14] that the concentration of excimer forming sites in a polymer film is controlled by the particular film coating conditions. Thermal treatment of

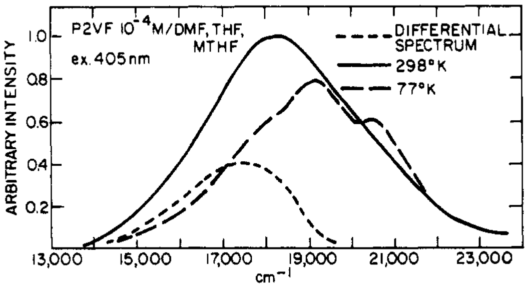

Figure 3. The total emission spectrum of a degassed 10^{-4} *M* solution of poly(2-vinylfluorenone) in a 1:1:1 mixture of THF, DMF, and MeTHF at 298°K (—), and 77°K (– –). The differential spectrum (---) was obtained after appropriate normalization at 21,500 cm^{-1}.

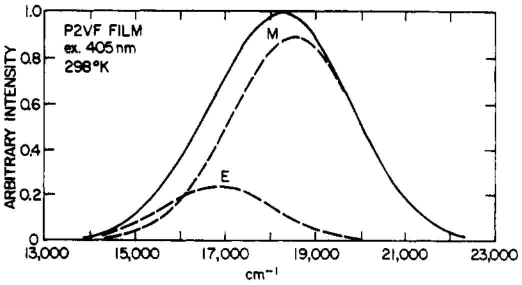

Figure 4. The 298°K total emission spectrum of a 3 μm film of poly(2-vinylfluorenone) on quartz. The excimer (E) and monomer (M) fluorescence subcomponents were obtained by a Gaussian curve resolving program. A standard deviation of 0.001 was obtained for the fit.

the P2VF films (heating to ~200°) followed by annealing or quenching at 77°K did not change the emission spectrum. T_g for P2VF is greater than 200° (and heating beyond this resulted in decomposition) and apparently this thermal processing did not provide enough freedom for the pendant fluorenone groups to modify the concentration of excimer sites enough to be detected by emission spectroscopy. Using the results from the solution studies, a curve fitting analysis (based on a Gaussian component band shape) was used to estimate the molecular and excimer contributions and these are included in Figure 4.

The dependence of fluorescence intensity upon incident light intensity is linear for P2VF both in solution and in films. This rules out delayed fluorescence arising from triplet–triplet annihilation processes. Furthermore, emissions observed in the fluorescent wavelength regions disappear when a rotating can is interposed between the sample and photomultiplier tube. For delayed fluorescence to be observed it would be required to have a lifetime shorter than 1 msec.

These results differ from those reported by Kearns[2] on zone-refined crystals of fluorenone. He reports a weak delayed emission coincident in wavelength with normal prompt fluorescence, and has attributed this emission to triplet–triplet annihilation processes.

Phosphorescence Emissions. Delayed emissions at energies lower than 17,500 cm^{-1} (~570 nm) have not been observed in solid solutions or films at 77°K. The origin of phosphorescence in fluorenone has been estimated[2,15] to occur near 17,800 cm^{-1}. Delayed emissions at long wavelengths have been reported by several workers[2,4–6] although none of these could be assigned unambiguously as phosphorescence. The absence of phosphorescence in P2VF is in agreement with results obtained by both Kearns[2] and Hunter[8] on fluorenone.

Previous workers[2,7] have observed that the fluorescence intensity of fluorenone is enhanced in polar solvents. Cohen and Guttenplan[16] also observed that the quantum yield of photoreduction of fluorenone in neat triethylamine is increased by a factor of 10 by dilution with cyclohexane, a nonpolar solvent, whereas dilution with 2-propanol or acetonitrile retarded the photoreduction. These results can be interpreted[7,8] as a solvent effect on the excited electronic states of fluorenone resulting in changes in the quantum efficiency of intersystem crossing. It was suggested that in polar solvents, an $^3(n,\pi^*)$ state originally between the lowest $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ state in energy is shifted to higher energy in nonpolar environments and exchanges position with a higher lying $^3(\pi,\pi^*)$ state.

The absence of phosphorescence in fluorenone and P2VF is understandable in polar environments, if this energy picture is correct, since El Sayed[17] has shown that transition probabilities between states of the same configuration are very small. Since the rigid glass solutions (TNF/MTHF/DMF in 1:1:1 ratio as solvent) of P2VF were very polar (a requirement for dissolving the polymer) no phosphorescence would be expected. The absence of phosphorescence in P2VF films suggests that this environment is also sufficiently polar to alter the energy levels and eliminate phosphorescence.

Attempts were made to populate the $^3(\pi,\pi^*)$ in P2VF via triplet–triplet energy transfer. 2,3-Butanedione was chosen as a donor, having a singlet excited state near 21,000 cm^{-1} and a triplet level near 19,200 cm^{-1}. Exciting a solution of 10^{-1} *M* 2,3-butanedione in the presence of 10^{-4} *M* P2VF at 436 nm, a wavelength totally absorbed in 2,3-butanedione, resulted in quenching of the long lived emission in the donor, and *no* sensitized phosphorescence in P2VF. Triplet–triplet energy transfer occurred thereby populating the $^3(\pi,\pi^*)$ state in P2VF, but neither phosphorescence nor delayed fluorescence was observed. On the basis of these results, the previous arguments relating to the inversion of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states are unnecessary. The absence of phosphorescence can be explained by radiationless decay from the lowest triplet state to the ground state which is faster than either radiative decay or triplet–triplet annihilation. There is no evidence from this present study to suggest that intersystem crossing is inefficient for P2VF in polar media, as has been proposed for fluorenone.

An "anomolous" phosphorescence with origin near 412 nm has been observed when P2VF solid solutions at 77°K are excited at wavelengths less that 325 nm. This emission is not observed when excitation wavelengths greater than 325 nm are used. The phosphorescence excitation spectrum (PE) yields an absorption spectrum that resembles P2VF for wavelengths less than about 340 nm.

The phosphorescence is highly structured having maxima at 412, 430, 440, 470, 482, 492, and 515 nm. The triplet state lifetime is 3.6 sec. Analysis of these bands suggests that emissions are occurring from at least two distinct species. The maxima near 412, 440, 470, and 515 nm correspond to the phosphorescence spectrum of benzophenone. The bands near 430, 480, and 490 nm are consistent with those expected for biphenyl and the observed triplet lifetime of 3.6 sec is identical with the lifetime for biphenyl.

One explanation for the photoproduction of benzophenone and biphenyl (or fluorene) in these systems is that excitation to the higher lying singlet state near 315 nm results in intersystem crossing to a higher lying triplet state which can undergo photochemical reactions. Fluorenone, or any ketone compound having a lowest lying $^3(\pi,\pi^*)$ state, may be photoreduced by amines via an electron transfer process. On the other hand, ketones having a low lying $^3(n,\pi^*)$ state undergo efficient hydrogen abstraction reactions.

Cleavage of the α carbon–carbon bond via the Norrish I process also occurs to some extent in these ketones.[18]

The formation of biphenyl may be explained on the basis of a Norrish I process followed by elimination of carbon monoxide and subsequent hydrogen atom abstraction. Benzophenone formation could occur via hydrogen abstraction by a $^3(n,\pi^*)$ carbonyl of a backbone C–H bond, scission of the five-membered ring, and subsequent free radical hydrogen atom abstraction. These reactions must, of course, occur from a higher lying $^3(n,\pi^*)$ state in order to explain the emissions from the triplet levels of biphenyl and benzophenone.

In conclusion, dilute solutions and thin films of P2VF exhibit normal and excimer fluorescence when excited in the lowest excited $^1(\pi,\pi^*)$ states. No phosphorescence from the lowest lying $^3(\pi,\pi^*)$ state is observed. Excitation of P2VF to higher excited singlet states results in photochemical reactions and possible formation of benzophenone and biphenyl, presumably from a higher lying $^3(n,\pi^*)$ state in P2VF.

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Laser Flash Photolysis Studies on Homo- and Copolymers of Phenyl Vinyl Ketone in Solution

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Received March 20, 1975

ABSTRACT: Triplet lifetimes τ of copolymers (CP) of methyl methacrylate (MMA), vinyl acetate (VAc), and styrene (St) with phenyl vinyl ketone (PVK) were determined as a function of PVK content in benzene solution at room temperature. Samples were irradiated with 347.1 nm light flashes. T–T spectra were recorded. With all three CP systems τ was found to increase with decreasing PVK content. The effect is most strongly pronounced with CP-MMA-PVK, where τ amounts to several microseconds at PVK contents of about 1 mol % (for homo PVK: τ = 0.1 μsec). In the system St/PVK τ increases only by a factor of ca. 2. The results are discussed in terms of triplet deactivation via 1,4 biradical formation and energy migration along the polymer chain. τ depends on CP concentration indicating self-quenching. Detailed kinetic studies performed with CP-MMA-PVK yielded the following results: assuming homogeneous distribution of PVK units in the solution the rate constant of intermolecular self-quenching amounts to $k_{\mathrm{s,inter}} = 7 \pm 1 \times 10^7$ l./base mol sec. Decay rate constants extrapolated to infinite dilution and determined for CP's with varying number of PVK units per chain yielded evidence for intramolecular self-quenching. τ decreases with increasing intensity of incident light, indicating triplet–triplet annihilation ($k_{\mathrm{T-T}} = 9.7 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$). Triplet quenching with 2,5-dimethylhexadiene-2,4 yielded rate constant values k_{q} between 7.5×10^8 and $9.5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ for CP's of all three systems studied. Oxygen also acted as a quencher. A fairly low rate constant $k_{\mathrm{O_2}} = 4.2 \pm 0.4 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ was estimated for CP-MMA-PVK (14.1 mol %).

Poly(phenyl vinyl ketone) (PPVK)[1-3,5] and copolymers of phenyl vinyl ketone (PVK) with styrene (St)[2,4] and methyl methacrylate (MMA)[4] are degraded in the main chain upon irradiation with uv light in solution. Generally, it is assumed that main chain rupture occurs in these cases via photoelimination according to a Norrish type II process involving essentially excited triplet states. A triplet state lifetime of about 100 nsec for homo-PPVK in benzene solution was determined in our laboratory recently.[6]

Golemba and Guillet[2] reported that on irradiating at λ 313 nm a copolymer of PVK and St (containing 9% PVK) a curved Stern-Volmer plot was obtained during the quenching of photoscissioning with 1,3-cyclooctadiene. This phenomenon was explained by assuming that either the triplet lifetimes of isolated PVK units are longer than those of excited PVK units neighbored by other PVK units or that the efficiency of quenching is greater for the copolymer than for the homopolymer. Lukáč et al.[4] also investigated the main chain degradation of copolymers of MMA and PVK and of St and PVK. They also assumed that triplet lifetimes of copolymers were longer than that of homo-PPVK and thought that the increase of triplet lifetime is responsible for the oxygen effect observed during the degradation of MMA/PVK copolymer.

Those considerations[2,4] appeared to become very important recently for our investigations on time-resolved measurements of chain scissioning using the light-scattering detection method[5] (data pertaining to the copolymers studied during this work will be reported later). We, therefore, started a quantitative study aimed at the determination of triplet lifetimes as a function of copolymer composition with three copolymer systems (MMA/PVK, St/PVK, and vinyl acetate (VAc)/PVK). In addition rate constants of inter- and intramolecular self-quenching, of triplet–triplet annihilation, and of reactions with certain quenchers were measured. These determinations became possible since the triplet lifetimes of copolymers were found being significantly longer than in the case of homo-PPVK.