End Injection of Triplet Electronic Excitation Energy into a Polymer Molecule Using Chromophores Bound at Chain Ends

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ABSTRACT: Polystyrene molecules labeled at opposite ends with naphthalene and aromatic carbonyl (AC) groups were prepared and their triplet photophysical properties investigated. By use of excitation at 337 nm the aromatic carbonyl was photoexcited selectively and time-resolved phosphorescence spectra were recorded at delay times from 100 μs to 100 ms. The AC phosphorescence was inhomogeneously broadened at the shortest delay times but becomes narrow and more structured with increasing delay time at 77 K. At ambient temperature the spectrum remains broad and structureless even at long delay times. Using dye laser excitation at 360 nm a narrow structured band is observed even at 150 μs after the excitation pulse. Energy transfer to the naphthalene group occurs efficiently and may take place either by direct transfer from excited AC groups or by an indirect process involving backbone phenyl groups. Electronically excited phenyl groups are thought to be produced by energy transfer from that set of triplet AC chromophores lying at the high-energy edge of the inhomogeneously broadened manifold. The resulting emission spectrum suggests the possibility of exciplex formation.

Introduction

The characteristics of excited electronic states of chromophores depend not only upon their intrinsic chemical makeup but also upon the environment in which they are placed. A case in point is the inhomogeneous broadening observed for molecules in substitutionally disordered crystals.[1,2] The spectral diffusion found in glassy benzophenone at low temperatures provides another example.[3] It has also been observed that chromophores such as naphthyl or carbazolyl exhibit somewhat different triplet photophysical properties when present as pendant groups on a polymer backbone than they do as isolated molecules.[4,5] In connection with investigations in this laboratory of triplet exciton migration in polymeric systems, an interest arose concerning the photophysical properties of chromophoric groups covalently bonded at the end positions of a polymer chain. It was anticipated that a pulse-probe method could yield useful information by selective excitation of a species which we shall label D (for donor) on one end of a chain while another chromophore, labeled A (for acceptor), is bonded at the other end of the chain. An approach such as this was pioneered and extensively explored by Winnik and coworkers in connection with photochemical reactions of functional groups placed at terminal positions of flexible polymer chains.[6] Mita et al.[7] have used polystyrene labeled at a single end to investigate rates of diffusion-controlled processes of these polymers in solution. The frequency of end-to-end collisions of polystyrene molecules labeled at each end with anthracene groups was studied by Horie et al.[8]

In the present case we wish to take advantage of monochromatic laser excitation and have considered only A species that cannot be directly photoexcited by the laser pulse used to excite D. That is, the first excited singlet state of D must lie lower in energy than that of A. On the other hand, the energy of the lowest triplet state of A must lie below that of D. One such pair, which turns out to be readily synthesized, involves the aromatic carbonyl as D and the naphthyl group as A. The polymer chain to which these units are attached was chosen to be polystyrene. Using PS to symbolize the polystyrene chromophore, these polymers would be represented as A-$(PS)_n$-D.

The process of triplet sensitization involving polymer molecules has been investigated by a number of research groups. In some cases small molecules have been used to sensitize polymers[9,10] and in others polymers have been used to sensitize small molecules.[11] In the present case one could envision the D to A process occurring by several different routes. One of these would be the direct intramolecular process in which the polymer coil achieves a configuration that happens to place the electronically excited D within a reasonable transfer distance from A. Another would be the intermolecular process where an excited D on polymer molecule 1 transfers its energy to a ground state A on polymer molecule 2. In principle, of course, the relative importance of these mechanisms could be assessed by dilution studies. A third process, which at first seems far less likely, would involve energy transfer from D to a PS unit followed by energy migration among the phenyl groups along the polymer chain until an A group is encountered. The reason this appears to have lower priority is because the energy level of the lowest triplet state of the phenyl group of polystyrene[12] is at 28 000 cm^{-1} whereas that for the aromatic carbonyl[13] is 26 000 cm^{-1}. This energy mismatch means that only a small fraction of aromatic carbonyl chromophores will, in principle, possess sufficient energy, even at ambient temperature, to make this channel a particularly viable one. It is important to recognize, however, that this statement is valid only if the energetics for these isolated chromophores also apply to similar chromophores bonded at the terminus of a polystyrene chain.

As noted above, however, alterations in the magnitude of the chromophore electronic state energies as a result of environmental effects are certainly not without precedent. In the present paper we will describe an unusual example of this effect involving both the naphthyl and aromatic carbonyl chromophores. In effect, it will be seen that a significant number of the aromatic carbonyl chromophores emit phosphorescence that is significantly higher in energy than that usually ascribed to the lowest triplet state of this species. The end result of this unusual environmental effect is that the triplet energy transfer mechanism, involving migration of the triplet exciton along the polystyrene chain segments, emerges as a viable one.

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Experimental Section

A. Polymer Preparation and Purification of Chemicals. Special styrene polymers were synthesized having different chromophoric groups at the terminal positions. As described above, these consist of the naphthyl group at one end and the phenylcarbonyl at the opposite end. The polymers were prepared by anionic polymerization using tetrahydrofuran (THF) as solvent. Reactions were carried out in a glovebox that was continuously purged with dry, oxygen-free nitrogen. The reaction sequence involved the initial formation of a 2-methylnaphthalide anion by the reaction of *n*-butyllithium with 2-methylnaphthalene. Styrene monomer was then introduced and polymerization was allowed to proceed for about 1 h. The reaction was terminated by adding benzaldehyde. The resulting terminal alkoxide ion is subsequently protonated to form a terminal alcohol. The polymer is purified by reprecipitation using benzene as solvent and methanol as nonsolvent.

The terminal hydroxide is oxidized to a carbonyl group by reaction of a slurry of the polymer in methylene chloride using pyridinium chlorochromate.[14] In a typical reaction, 1.3 g of polymer was dissolved in 25 mL of CH_2Cl_2 while 2.55 g of pyridinium chlorochromate was suspended in 25 mL of CH_2Cl_2. The polymer solution was added to the suspension and the mixture was stirred for 2–3 h after which the methylene chloride was evaporated leaving a brown-black residue. The residue was extracted several times with diethyl ether and the collected extracts were filtered through a bed of Celite. The diethyl ether was then evaporated to recover the polymer. The polymer was dissolved in benzene and reprecipitated by using methanol. This was considered to be the crude polymeric product.

This crude product was subjected to additional purification using a procedure recently developed in these laboratories based upon silica gel column chromatography.[15] A slurry of 20 g of silica gel (10% water content) with HPLC grade cyclohexane was made and packed into a column. The crude polymeric product was dissolved into the minimum amount of cyclohexane and added to the column. Next, 20 mL of cyclohexane was passed through the column followed by 100 mL of 70% (v/v) benzene in cyclohexane. Twenty-five-milliliter portions of the benzene/cyclohexane mixture were collected and each was monitored by using thin layer chromatography to identify those containing the purified polymer. The purified polymer was finally precipitated once more with methanol before being dried overnight at ambient temperature under vacuum.

In this way a group similar to acetophenone is produced at the terminus and, of course, the naphthalene initiating group is present at the opposite end. Other polymers were prepared having a single end cap consisting of either the naphthalene chromophore or the acetophenone-like (AC) chromophore. All of these syntheses used the same anionic procedure described above with the elimination of the appropriate step to achieve the particular single terminating group desired. Additional purification of the polymers was carried out by using a silica gel column and benzene/cyclohexane mixed solvents as eluant.

The polymer molecular weights were determined by analytical ultracentrifugation. A Beckman Model E ultracentrifuge was used. It was equipped with a UV/vis monochromator and an optical scanner interfaced to a 12-bit high-speed A/D converter connected to a microprocessor. Runs were conducted at 18–20 °C using rotor speeds from 18 000 to 30 000 rpm. Times to equilibrium varied from 6 to 24 h. Raw data were analyzed by using locally developed software. Plots of log (concentration) versus the square of the distance from the rotation axis to the probe point were prepared and found to be linear for all samples, indicating a high degree of monodispersity and the absence of significant quantities of oligomeric material. Two different double-capped polymer samples labeled DCPS1 and DCPS3 were used for essentially all of the work reported here. Their molecular weights are respectively 6740 and 2240 Da.

Further characterization of these polymers involved the detection of the appropriate luminescent species, that is, AC and naphthalene, by photoexcitation of the samples. These experiments will be described in detail below. In addition, UV absorption spectra of the polymers showed the presence of weak bands at 320 and 305 nm plus strong absorption at 280 nm. In addition, the naphthalene-capped polymer shows a weak band at 311 nm. Published absorption spectra[16] of 2-methylnaphthalene show a sharp but weak band at 319 nm, which falls off rapidly to zero at lower energies. Two other weak bands are also reported at 311 and 305 nm. Thus, the absorption spectra recorded here are consistent with the presence of the alkylnaphthalene group. Published absorption spectra of acetophenone[17] show a shoulder near 320 nm, which falls gradually to zero near 350 nm. The molar absorptivity of this band is ten times smaller than that of the overlapping band from 2-methylnaphthalene and so the presence of AC groups cannot be confirmed from absorption spectra alone. On the other hand, the AC chromophore still possesses nonzero oscillator strength at 337 nm, the nitrogen laser line, whereas the sharp cutoff of the 2-methylnaphthalene absorption at wavelengths above 320 nm suggests that negligible absorption by this species will occur using the nitrogen laser. From the known molecular weights of the polymers and the known concentration of naphthalene chromophores as deduced from absorption spectra, it was found that typically 20% of the polystyrene chains are labeled with naphthalene.

In the course of this work it became necessary to evaluate emission spectra of samples dispersed in polymer matrices. Poly(methyl methacrylate) (PMMA) was chosen as the matrix material since it was assumed it would be inert to any of the triplet processes being studied. Commercially available samples of PMMA were found to produce phosphorescence emission in a range overlapping those of interest and so it was decided to prepare the polymer in the laboratory under carefully controlled conditions. An anionic polymerization was selected in which *tert*-butyllithium served as the initiator. The polymerizations were carried out in a nitrogen atmosphere in the glovebox at −80 °C. When the polymerization was completed (after about 48 h) methanol was added to quench anions and to precipitate the polymer. The polymer was further purified by repeated reprecipitations using benzene as solvent and methanol as nonsolvent. Even these carefully prepared samples of PMMA produced a very weak phosphorescence emission with a maximum at 450 nm. Because the emission was quite weak and because it appeared at a position that did not interfere with either the AC or naphthalene phosphorescence, it was used as a matrix material for some the spectra reported below.

The THF was treated by passage through an activated alumina column followed by distillation away from calcium hydride and then phosphorous pentoxide. It was finally distilled from a sodium–potassium alloy with a small amount of benzophenone added as a color indicator to show dryness. Styrene and methylnaphthalene were distilled under vacuum prior to use. Naphthalene was recrystallized from ethanol and was zone refined by 100 passes in a zone melting apparatus. Propiophenone (Fluka purum grade) was used as received and 3-phenylpropiophenone (Pfaltz and Bauer) was treated by passage through a silica gel column followed by three recrystallizations from ethanol.

B. Spectroscopic Apparatus. The different spectroscopic systems used in this work can be characterized as using either conventional light sources or else laser systems. The one using a conventional source is a phosphorimeter utilizing a Hg–Xe excitation lamp with mechanical choppers on the emission and excitation beams. Emission signals are detected by a photomultiplier after passage through a monochromator. Signals are recorded on a signal averager and relayed to computers for analysis. Details of this apparatus have been published elsewhere.[18] The laser-based systems have also been recently described in the literature.[19] They consist of a XeCl excimer laser used either directly or as a pump source for a dye laser. The XeCl laser may also be operated with a nitrogen fill gas for operation as a nitrogen laser.

A tunable dye laser was also employed in this work. The instrument used was a Lambda Physik FL 2002 dye laser pumped with the XeCl excimer laser. The dye used was purchased from Lambda Physik and has the commercial name DMQ. It is useful in the wavelength range from 346 to 377 nm. It was tuned for use at 360 nm, which is at the lower energy edge of the absorption band of the aromatic carbonyl group.

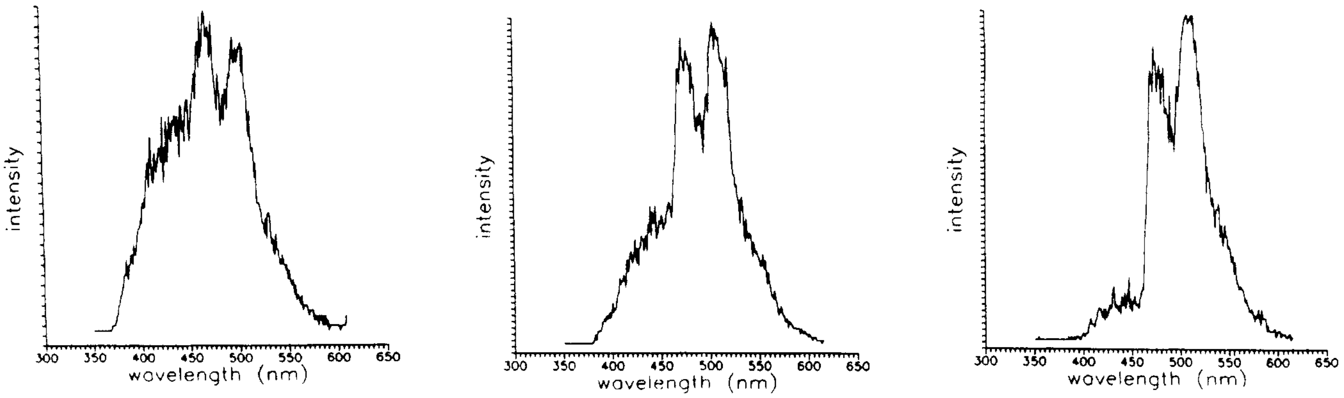

Figure 1. Phosphorescence spectra of a double-capped polymer in MTHF at 77 K with XeCl laser excitation at different delay times. From left to right delay times are 95, 190, and 750 ms.

The emission beam is focused on the slits of a monochromator and the signal is detected by a photomultiplier. It is then preamplified and inverted before being sent to the signal averager. All data analyses including spectral displays are carried out by computer methods.

Experimental Results

Spectroscopic Experiments. Time-resolved delayed emission spectra of DCPS3 are presented in Figure 1. Here excitation was provided by the XeCl laser and rather long delay times were used in order to emphasize the naphthalenic portion of the emission. The spectra consist of two emission envelopes that overlap: 370–470 and 470–600 nm. These are identified as being produced from AC and naphthyl groups, respectively. Note that as the delay time increases the relative intensity of the AC portion of the emission band decreases, leaving essentially the isolated naphthyl group phosphorescence. No essential difference between spectra of DCPS3 or DCPS1 were noted. Also, phosphorescence spectra of solid films of these double-capped polymers recorded under similar conditions but at ambient temperature yield only the naphthalenic emission. Presumably quenching and first-order relaxation processes are significantly faster for the AC chromophore at elevated temperatures. The phosphorescence spectrum of a polymer chain capped only with the naphthalene group was also recorded by using excitation with the XeCl laser. It appears very similar to that of Figure 1 at long times after the excitation pulse.

The appearance of the time-resolved spectra for double-capped polymers creates the impression that the naphthalene emission is growing with increasing delay time. This is, of course, not the case in the time range covered by these spectra. The impression is due to the fact that the naphthalene component is decreasing at a lower rate than the AC component and each spectrum is normalized for full-scale deflection of the most intense peak. This comment applies to all of the time-resolved spectra recorded here.

Figure 2 displays time-resolved delayed emission spectra of DCPS1 in a rigid MTHF glass at 77 K, using nitrogen laser excitation at 337 nm. Here the spectra are recorded by using much shorter delay times of 0.1, 1.0, 10, and 100 ms after the excitation pulse. The time evolution clearly shows the presence of predominantly AC emission at short times (0.1 and 1.0 ms) and the emergence of a second band centered at 510 nm at longer times. The long-wavelength emission appears first as a shoulder (1.0 ms), then as a bona fide emission envelope (10 ms), and finally as the dominant spectral characteristic at very long times (100 ms). If we focus on the AC emission for a moment, we see that at short delay times (0.1 ms) the emission is broad and structureless, ranging typically from 350 to 470 nm. On the other hand, at longer delay times the emission is not as broad, ranging from 380 to 470 nm, and is now structured with three prominent peaks at 396, 418, and 448 nm.

The emission at 510 nm would seem, by default, to be associated with naphthalene; however, it does not have the vibronic structure expected for this chromophore as seen in the spectra of Figure 1 where the naphthalene has been directly photoexcited. On the other hand this 510-nm component does appear to be similar to the phosphorescence of the naphthalene excimer as found, for example, in spectra of solid films of poly(2-vinylnaphthalene). Additional observations about the origin of this emission band will be presented below, but in the meantime, we will refer to it as a naphthalene emission.

It is worth mentioning that time-resolved phosphorescence spectra for a mixture of propiophenone (9.1×10^{-3} M) and naphthalene (1.0×10^{-2} M) in MTHF at 77 K are quite different from these polymer spectra. For mixtures of these small molecules, with 337-nm excitation, there is only the AC type of phosphorescence at delay times as large as 100 ms. Only at very long times after excitation, on the order of several hundred milliseconds, does one observe luminescence due to naphthalene. Furthermore, the naphthalene spectrum, when it finally does appear, is the typical monomeric emission complete with vibronic structure. When the naphthalene concentration was increase by a factor of 7.5 the results were essentially the same.

An example of the delayed luminescence spectrum of a solid film is presented in Figure 3. As in the previous spectrum, this one is recorded at 77 K and the nitrogen laser has been used for excitation. Once again it is presented in a time-resolved fashion at delay times of 0.5, 1.0, 10, and 50 ms. The location of spectral peaks and their time evolution are seen to be very similar to that observed for the rigid solution. In particular it is noteworthy that the AC portion of the emission extends down to 350 nm at the shortest delay time after excitation. At a delay time of 1 ms, however, the AC portion of the emission has narrowed considerably and exhibits the structural features commonly associated with this chromophore.

At ambient temperature, the time evolution of these phosphorescence bands takes on a somewhat different character as exhibited in Figure 4. This is a delayed luminescence spectrum of a solid film of DCPS3 recorded by using 337-nm excitation from the nitrogen laser. Here, after a delay time of 1.0 ms, the AC portion of the spectrum is very weak compared with the naphthalenic com-

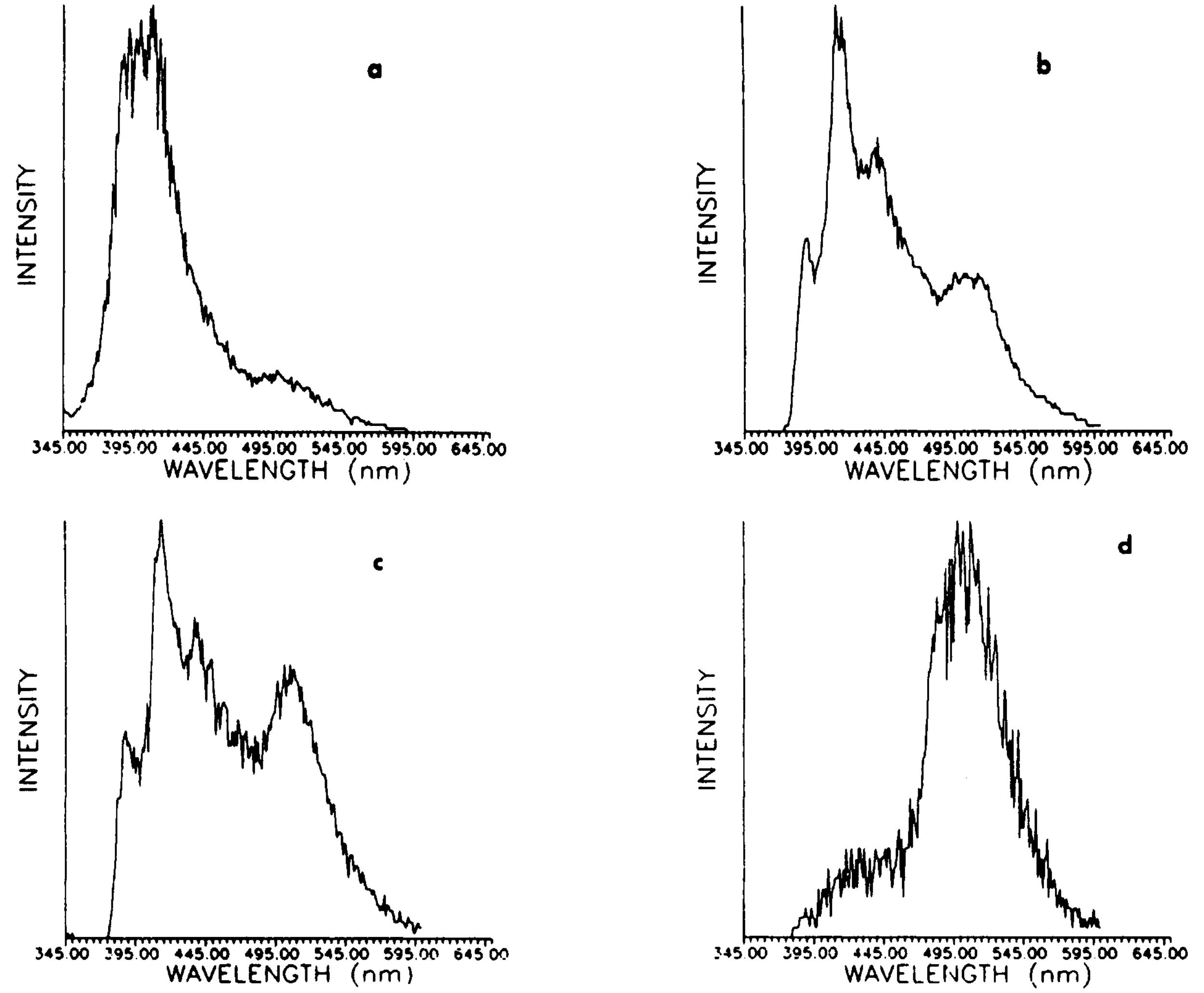

Figure 2. Time-resolved phosphorescence spectra of a double-capped polymer in rigid MTHF solution at 77 K excited by using 337-nm light. Delay times are 0.1, 1.0, 10, and 100 ms for a–d, respectively.

ponent. Furthermore, the AC component does not appear to undergo the band narrowing with emergence of structural features typical of its behavior at 77 K. It may also be noted that the naphthalenic portion of the emission band also retains an essentially structureless character even at the longest delay time of 10 ms.

To explore further the behavior of the AC part of the emission envelope, delayed luminescence spectra were also recorded for a polymer that had been synthesized having only the AC end cap but not the naphthalenic one. The acronym ACPS is used for this sample. Figure 5 is a delayed luminescence spectrum of the ACPS species recorded at 77 K using nitrogen laser excitation at 337 nm and at different delay times after the excitation pulse. Here we see behavior similar to that found for the double-capped polymers in that the emission band initially extends down to 360 nm but then narrows so that its origin is at 385 nm at a delay time of 1.0 ms. The vibronic components of this band are also seen to emerge at longer delay times. Similar experiments were conducted with poly(methyl methacrylate) as the matrix medium rather than a solid neat film. In this case spectra were also recorded at 77 K and found to display the band narrowing with increasing delay time similar to that seen in Figure 5.

In Figure 6 one sees a delayed luminescence spectrum recorded under the same conditions as used for Figure 5 except that the temperature is 298 K. At this elevated temperature no band narrowing and no emergence of structured luminescence is found even at relatively long times after the excitation pulse.

It was assumed that a major contributor to the band broadening observed in these phosphorescence spectra was the inhomogeneous environment in which individual chromophore groups are located. An independent way to test for this effect involves excitation at a low-energy band edge in order to produce a set of excited-state species that lie at the low-energy side of the inhomogeneous distribution of excited states. One would expect to observe structured phosphorescence spectra even at short delay times using this sort of selective excitation. An attempt was made to carry out such an experiment at ambient temperature by using 360-nm excitation from the tunable dye laser. Unfortunately, the number of excited states produced was too small to produce a reasonable emission spectrum. At 77 K, however, by use of a short delay time of 150 μs, which would have produced a broad spectrum with 337-nm excitation, a highly structured spectrum is obtained by using 360-nm excitation from the dye laser as is illustrated in Figure 7.

In order to assess the behavior of individual molecules that are not bonded to a chain backbone, time-resolved phosphorescence spectra were recorded for propiophenone and 3-phenylpropiophenone in MTHF glass at 77 K. The results for 3-phenylpropiophenone are presented in Figure 8 and are essentially the same as were found for propiophenone. In this case a structured band is observed even at a delay time of 0.1 ms. Although

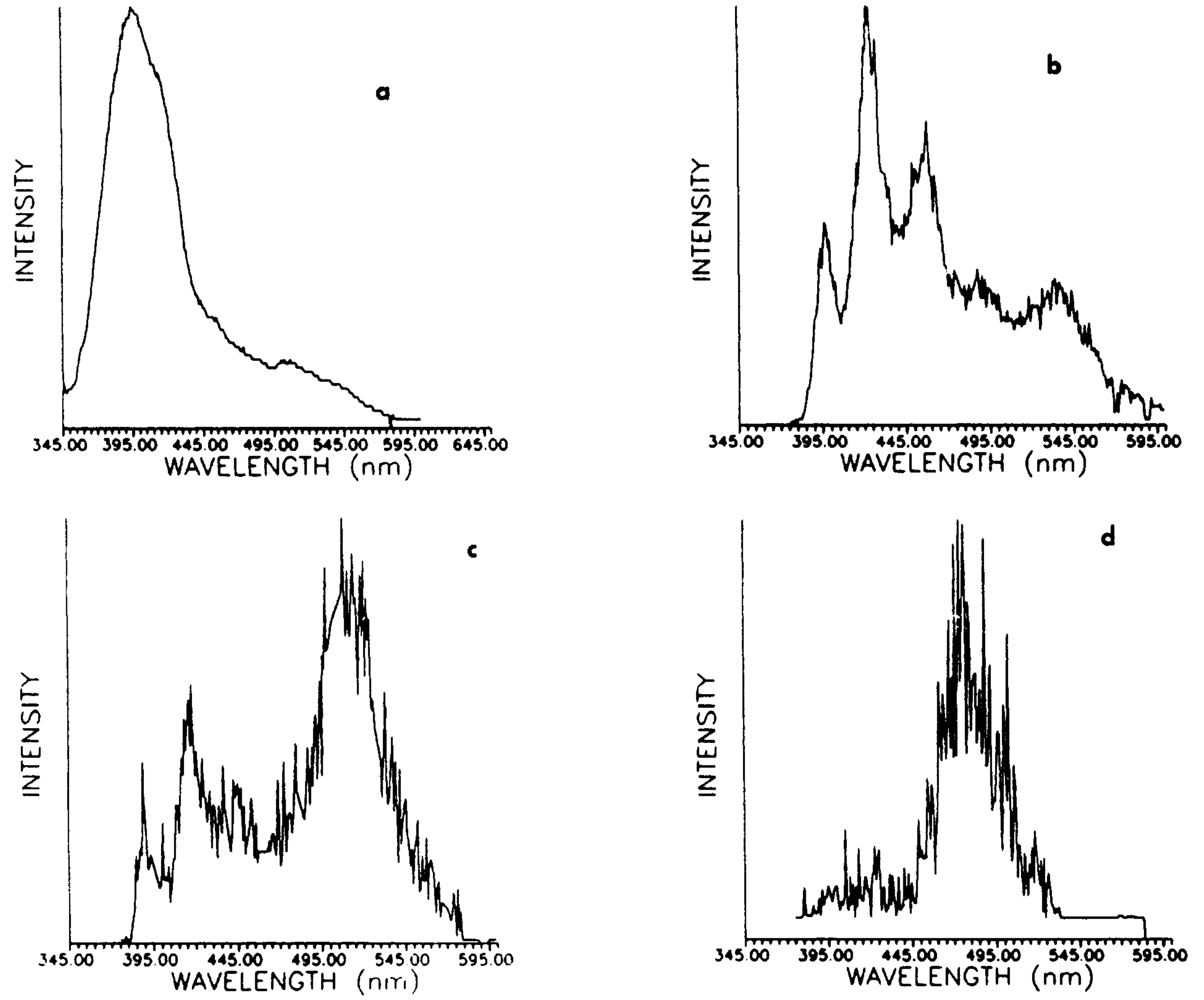

Figure 3. Time-resolved phosphorescence spectra of a double-capped polymer solid film at 77 K excited by 337-nm light. Delay times are 0.5, 1.0, 10, and 50 ms for a–d, respectively.

there is some indication of weak luminescence below 385 nm at the shortest delay time, it is much less intense than the emission in that same region from polymer-bound chromophores. Phosphorescence spectra were also recorded at 77 K for a sample of polystyrene that had been doped with propiophenone. Again, at a delay time of 0.1 ms, no broadening of the spectrum occurred and the vibronic components were well resolved.

Results of Luminescence Decay Kinetics. In general it was found that the phosphorescence decays, monitored across the spectral band, did not strictly obey a single exponential. Thus, the indication is that either there are processes occurring that are of higher order than unity or else the decays are multiexponential. At relatively long times after the excitation pulse single-exponential behavior is more closely approached and the lifetimes quoted below are determined for this long-time region by using a forced exponential fit. Lifetimes are quoted here from decays monitored at 420 nm to emphasize the AC component and at 550 nm to emphasize the naphthalene component. Also, the excitation source for these rate experiments was the nitrogen laser and, therefore, any naphthalenic groups present have been indirectly excited. Since the data differed very little for solid films versus frozen glassy solutions, they have been all averaged together for the experiments at 77 K. At ambient temperature lifetimes were measured only for fluid solutions in MTHF solvent. The results are collected in Table I.

Lifetimes were also monitored at 420 nm in solution and solid film for the polymer containing only the AC chromophore. They were essentially the same as those quoted above for the double-capped polymers. The lifetime for the naphthalenic portion of the phosphorescence emission from double-capped polymers was also determined by using XeCl laser excitation, that is, by using direct excitation of the naphthalene chromophore. In this case, the lifetime of the naphthalene triplet in MTHF at 77 K was found to be 1.9 s, which is very similar to triplet lifetimes found for the isolated chromophore at this temperature. Even in this case, however, a very short-lived component of the decay profile could be observed.

Since it was anticipated that the emission at 510 nm probably arises by way of energy transfer from the triplet AC species, it was initially thought that a rise time for this component might be observed at short times after the excitation pulse. In fact, it is not possible to obtain this information since the tail of the AC emission envelope, in the low microsecond time regime, extends beyond 510 nm and, at such short delay times, the naphthalenic emission is masked. Thus, these experiments were unable to confirm any time delay in formation of the secondary excited-state species.

Discussion

The time-dependent behavior of these spectra for experiments at 77 K versus those at ambient temperature is

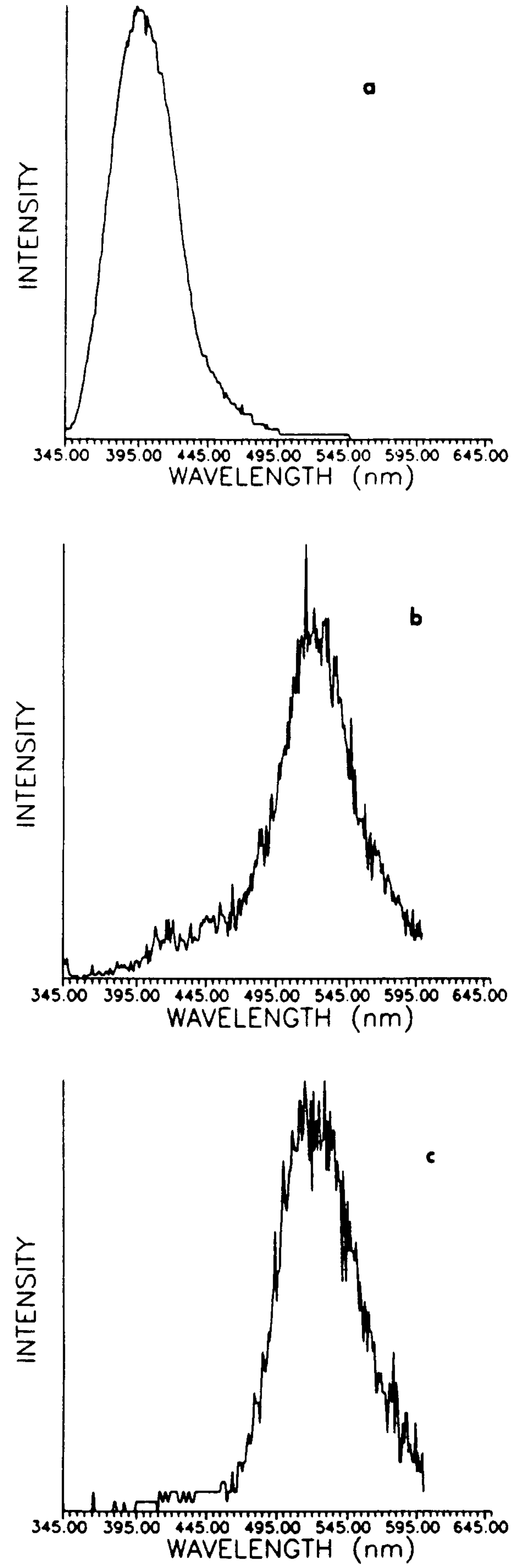

Figure 4. Time-resolved phosphorescence spectra of a solid film of the double-capped polymer at ambient temperature excited by using 337-nm light. Delay times are 0.1, 1.0, and 10 ms for a–c, respectively.

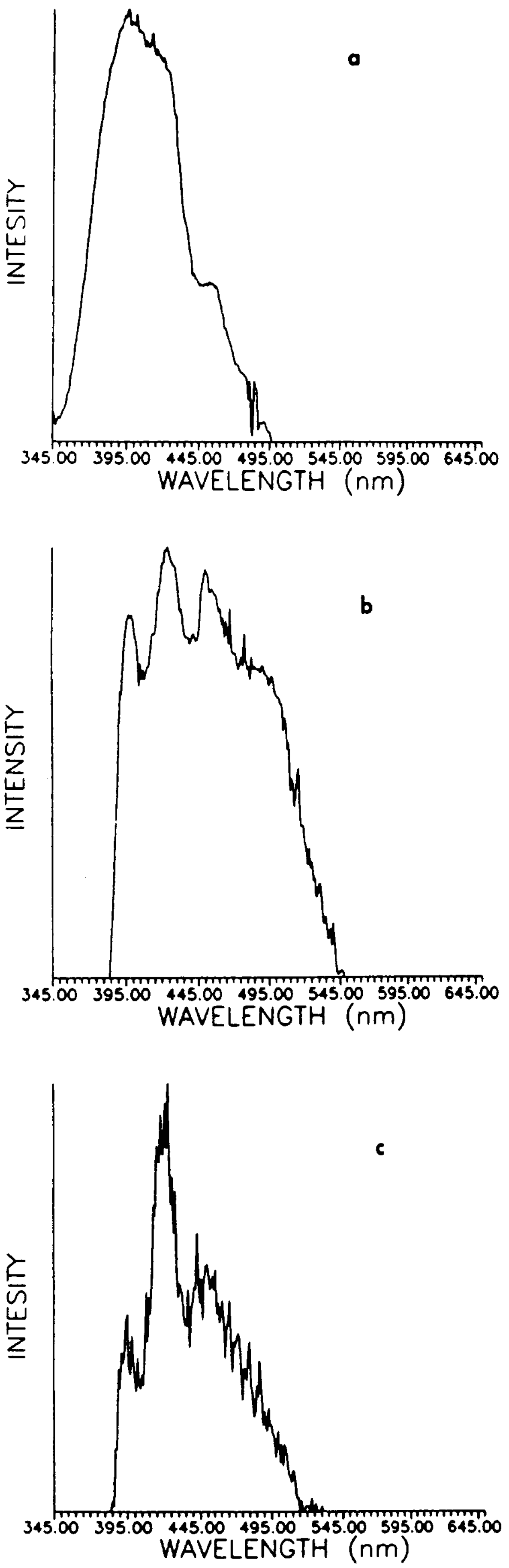

Figure 5. Time-resolved phosphorescence spectra of the AC-capped polymer solid film at 77 K excited with 337-nm light. Delay times are 0.1, 1.0, and 10 ms for a–c, respectively.

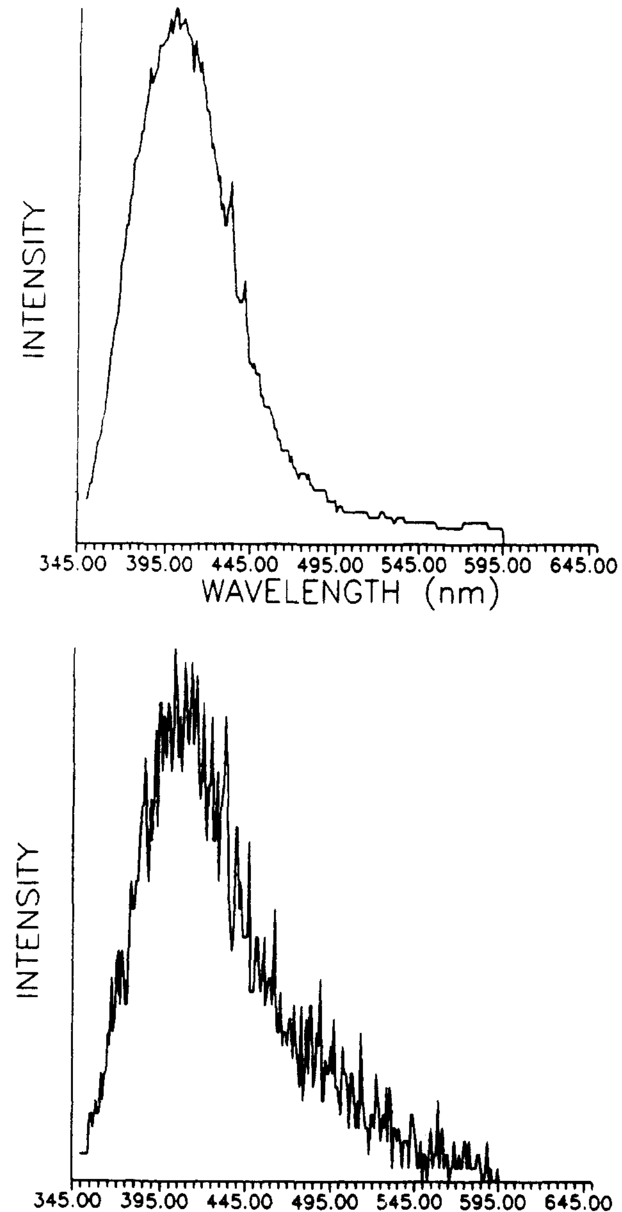

Figure 6. Time-resolved phosphorescence spectra of the AC-capped polymer solid film at ambient temperature excited with 337-nm light. Delay times are 0.1 (upper) and 1.0 ms (lower).

indicative of the existence of an inhomogeneous distribution of electronic states, which, in this case, are the triplet states responsible for phosphorescence emission of the AC chromophore. The physical processes that are operative in such systems have been described by various authors and most recently by Bassler and coworkers.[20]

The basis of the model, supported by the spectroscopic results, is that instead of chromophores existing in a single electronic state there are a multitude of closely spaced electronic states, the energy of which depends upon the particular environment experienced by the chromophore. The average value of the energy separation between these closely spaced states is called the inhomogeneous line width (σ). At temperatures high enough such that the Boltzmann factor, kT, is large compared to σ, the initial distribution of occupied states will not change appreciably over time and the emission profile at short times after the excitation pulse will closely resemble the profile at longer times. In this high-temperature limit there is a negligible hindrance for energy redistribution from a given state to other neighboring states that are either slightly higher or slightly lower in energy. It should be borne in mind that superimposed upon this thermodynamic setting is a kinetic one. For example, even if kT is smaller than σ, no change in spectral characteristics will be observed if the energy redistribution process occurs on a time scale that is much longer than the lifetime of the excited state.

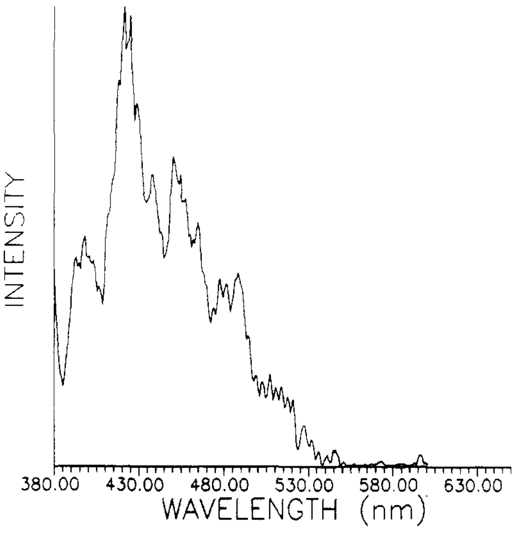

Figure 7. Phosphorescence spectrum of the AC-capped polymer solid film at 77 K excited by using a dye laser tuned to 360 nm.

At temperatures sufficiently low such that kT is small compared with the inhomogeneous line width, the direction of energy redistribution for a given electronically excited molecule will be constrained always to a lower energy state. This, of course, will lead to time-dependent changes in the emission spectrum if the energy redistribution occurs on a time scale that is small compared with the excited-state lifetime. In this case spectral shifts to lower energy emission are favored with increasing time. As emission events occur increasingly from the lower edge of the inhomogeneous distribution, the vibronic structure associated with vibrational states of the ground electronic state will begin to emerge. This scenario, which usually goes under the name of spectral diffusion, is, of course, exactly what is observed with the AC chromophore at 77 K. On the other hand, at ambient temperature no band narrowing and no emergence of structural features take place. The product, kT, is 209 cm^{-1} at 298 K and so it may be concluded that σ has this value as an upper limit.

Most observations of spectral diffusion have been made at much lower temperatures than those used here and we are aware of no previous observations of spectral diffusion for triplet emission in a polymeric system. The reason it is observable in the present case may be related to the kinetic aspects of the diffusion process. Although the exact mechanism for energy redistribution is not known, it presumably involves a combination of internal rotations about covalent bonds or else larger scale rotations of the entire chromophore. An alternative mechanism would involve triplet energy migration, presumably by electron exchange, from one chromophore to another.

In these polymers it is probable that the energy migration process will be retarded since each AC chromophore is necessarily in the immediate neighborhood of its own polystyrene chain and will therefore be somewhat shielded from neighboring AC species. Similarly,

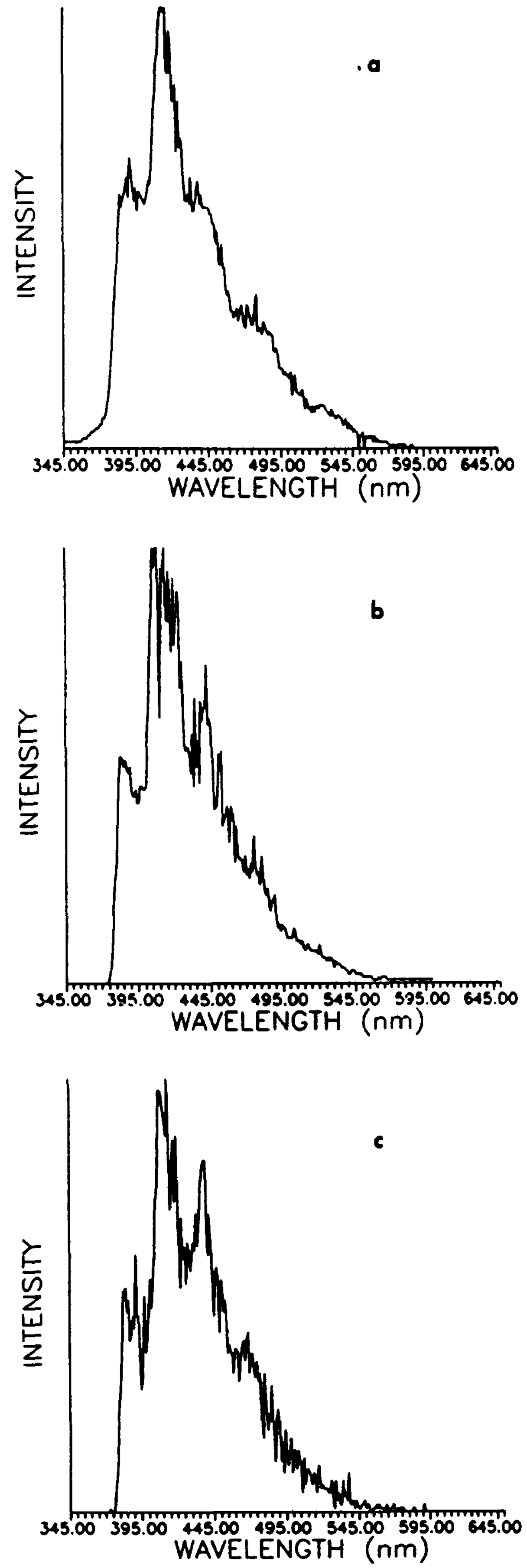

Figure 8. Time-resolved phosphorescence spectra of 3-phenylpropiophenone in MTHF at 77 K excited at 337 nm. Delay times are 0.1, 1.0, and 10 ms for a–c, respectively.

Table I
Lifetimes of Phosphorescence Decay for Double-Capped Polystyrene Polymers at 77 K and at Ambient Temperature Monitored at 420 and 550 nm

sample	wavelength, nm	temp, K	av lifetime, ms
DCPS1	420	77	2.2 ± 0.1
DCPS3	420	77	2.1 ± 0.4
DCPS1	550	77	4.2 ± 0.8
DCPS3	550	77	4.6 ± 0.6
DCPS1/DCPS3	420	ambient	0.16 ± 0.03
DCPS1/DCPS3	550	ambient	0.12 ± 0.03

large-scale rotational motions will be retarded since the polystyrene chain will be imbedded in the surrounding lattice. This situation may be contrasted with, for example, the vitreous benzophenone samples studied by Bassler and co-workers[3] or the substitutionally disordered crystals studied by Morgan and co-workers.[1,2] In these latter two cases, spectral diffusion was observed at temperatures on the order of 4.2 K and energy migration was definitely implicated as the primary mode of energy redistribution.

For the small molecule analogues, propiophenone and 3-phenylpropiophenone, only a slight indication of spectral diffusion is observed at the smallest delay time of 0.1 ms as seen in Figure 8. It was, in fact, surprising to observe any indication at all of spectral diffusion for these small molecules. Apparently the process is more rapid here than in the polymer-bound system.

One way to verify that these time- and temperature-dependent spectral changes are due to spectral diffusion is to use an excitation beam tuned to excite only a small population of chromophores at the lower edge of the energy band. In this way it is expected that even at short times after the excitation pulse the emission spectrum will display a more structured aspect than one in which broad-band excitation has been used. These expectations are, in fact, borne out when a dye laser tuned for excitation at 360 nm was used as is seen in Figure 7.

Let us now explore the characteristics of the portion of the emission spectrum that has, in the foregoing, been attributed to the naphthalene triplet state and exhibits an emission maximum at 510 nm. The following observations are relevant in the interpretation of this phosphorescence signal.

(1) When either the double-capped or the naphthalene-capped polymers are photoexcited at 77 K by using the XeCl laser, the resulting phosphorescence band is clearly due to naphthalene. Both the lifetime and spectral characteristics of these bands are consistent with those expected for the naphthalene species.

(2) When 337-nm excitation is used, the emission found in this region of the spectrum is similar to that expected for the triplet excimer of naphthalene.

(3) No emission at 510 nm is observed from polymers that do not contain a naphthalene cap.

(4) The lifetimes of the AC emission and of the naphthalenic one are very similar both at 77 K and at ambient temperature when 337-nm excitation is used.

(5) A mixture of small molecules, propiophenone and naphthalene, when photoexcited by 337-nm light at 77 K in an MTHF glass produces only AC emission up to delay times of 100 ms. Monomeric naphthalene phosphorescence is found when the delay time is increased to 500 ms or greater but no emission at 510 nm is produced.

(6) At a delay time of 100 ms after 337-nm excitation the double-capped polymer yields a spectrum consisting predominantly of the 510-nm emission. At the same delay

time the phosphorescence spectrum of the small molecule mixture is still exclusively that of the aromatic carbonyl.

From points 2 and 3 one may conclude that the emission at 510 nm involves a species that includes naphthalene as a component and that it is probably an excited-state complex. It seems unlikely, however, that the species could be a naphthalene excimer. First of all, the lifetime of this emission band is only about 4 ms, whereas that expected for the naphthalene excimer would be on the order of a second. Second, the system is very dilute in naphthalene chromophores and the probability that two of them will be found in an appropriate spatial arrangement for excimer formation is very small indeed. Finally, if excimers were being formed, one would expect to find excimeric phosphorescence with direct excitation as well as indirect excitation.

If an excited-state complex is being formed here and if an excimeric species is not likely, then consideration should be given to the existence of an exciplex. For example, a process such as

$$^3\mathrm{AC}^* + {}^1\mathrm{N}_0 \rightarrow {}^3\mathrm{Ex}^*$$

could take place where $^1\mathrm{N}^0$ represents the naphthalene ground state and $^3\mathrm{Ex}^*$ is a triplet exciplex. Not many observations of triplet exciplex formation have been reported, but one well-characterized case involving acetone and durene has recently been discussed by Johnston et al.[21] It is probable that only a small number of naphthalene groups would be situated properly to interact with the AC portion of the chain and this would account for the relatively small intensity of the 510-nm emission.

Another mechanism to account for the 510-nm signal is suggested by the fact that the phosphorescence emission from AC species at short delay times extends to wavelengths below 350 nm. Thus, the energy of those aromatic carbonyl chromophores that are at the high-energy edge of the triplet manifold is sufficient to sensitize neighboring phenyl groups. Since triplet excitation can, in this way, be injected into the polymer at a chain end, interaction between triplet phenyl groups and ground-state naphthalene could be responsible for the 510-nm emission observed. From point 5 above it is apparent that the simple mixing of naphthalene and an aromatic carbonyl does not result in the production of the 510-nm signal. Their connection via the covalent bonds of the polymer chain is evidently necessary either because of the guaranteed proximity that results or because of the presence of phenyl groups, which are potential energy acceptors. For the solution of small molecules that was studied here consisting of propiophenone (9.1×10^{-3} M) and naphthalene (1.0×10^{-2} M) in MTHF the average intermolecular distance is 24 Å. For the larger of the two double-capped polymers the root-mean-square end-to-end distance, $\langle r^2 \rangle^{1/2}$, is 17 Å and for the smaller it is 10 Å. Thus, if effects of proximity were of paramount importance the 510-nm emission should have been observed in this concentration solution of small molecules. It may be concluded, therefore, that the polymer system exhibits distinctive photophysical behavior for two reasons. First of all, the triplet state of the polymer-bound AC chromophore is sufficiently broadened so that energy transfer to backbone phenyl groups is energetically allowed. Second, triplet energy migration among backbone phenyl groups provides an indirect route for quenching by polymer-bound naphthalene groups.

On the question of potential impurities being responsible for some of the emission signals observed here, it may be pointed out that the same purification procedures were used for polymers made with and without naphthalene terminating groups. The method of purifying these samples consisted not only of multiple reprecipitations, which is the most popular method of purification, but also utilized the silica gel column method, which is particularly effective in ridding the samples of small molecule impurities. This latter technique has even proved effective in removing luminescing impurities from commercial samples of polystyrene, which is notoriously difficult to accomplish. In spite of these efforts it is, of course, always difficult to dispose of the possibility of interference from impurities with absolute certainty.

Conclusions

The broad phosphorescence band emitted by acetophenone-like chromophores bound at a polystyrene chain end is a result of inhomogeneous broadening resulting from a variety of environmental conditions in which the chromophore may be found. The usual structured phosphorescence may be observed from frozen solutions at 77 K or from solid films at 77 K either by using an excitation source tuned to coincide with the low-energy edge of the absorption band or by using delay times after the excitation pulse of greater than 1 ms.

Rate experiments suggest that energy transfer from excited AC chromophores to ground-state naphthalene groups occurs either by a direct process or by energy transfer from triplet AC chromophores at the high-energy edge of the inhomogeneous band to backbone phenyl groups. Subsequent energy migration among phenyl groups along the chain backbone ultimately leads to quenching when a naphthalene group is encountered. The rapid decay of the exciplex-like emission may be a result of a small intrinsic lifetime coupled with a significant rate of dissociation. Since the polymeric system exhibits photophysical behavior that is quite distinct from that found for a mixture of small molecules consisting of the same chromophoric species, it is concluded that the extensive inhomogeneous broadening of the AC emission in the polymeric system is primarily responsible for its singular behavior.

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Copolymerization of Hexafluoroisobutylene and Vinyl Acetate

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ABSTRACT: Alternating copolymers of hexafluoroisobutylene (HFIB, monomer B) and vinyl acetate (VA, monomer A) were prepared under homogeneous radical conditions, and their structures were studied. The microstructure of the copolymers was studied by proton, carbon-13, and fluorine NMR. Monomer reactivity ratios were determined by a nonlinear least-squares procedure and from an analysis of the sequence distributions. The results support a penultimate model in which $r_{aa} = 0.0066$, $r_{ba} = 0.0405$, and $r_{bb} = r_{ab} = 0$. Configurational studies indicated that the stereochemistry of the alternating copolymers is not random and the tacticity is related to polymerization temperature. Bulk properties of the copolymers were examined by DSC, dielectric relaxation, and the XRD method. Alternating copolymers of HFIB and vinyl alcohol were also prepared.

Introduction

Although hexafluoroisobutylene (3,3,3-trifluoro-2-(trifluoromethyl)propene, referred to as HFIB or monomer B) and its copolymer with vinylidene fluoride (VDF) are now commercially available,[1] little is known about the polymerization behavior of HFIB and the microstructure of its copolymers. Infrared,[2] dielectric relaxation,[3] and X-ray diffraction[4] studies of the HFIB-VDF copolymer have been reported, indicating the crystalline and alternating nature of this copolymer. The scarcity of detailed NMR work on this copolymer is mainly due to its insolubility in solution.

NMR is a powerful tool for studying the microstructures of polymers.[5,6] For this purpose a soluble copolymer of HFIB is desirable. We report here the preparation of an amorphous and soluble copolymer of HFIB with a nonfluorinated vinyl monomer and a study of the microstructure of this copolymer. Vinyl acetate (referred to as VA or monomer A) was chosen since it readily copolymerizes with fluoroolefins[7] and since most of its copolymers, such as those with vinylidene cyanide (VDCN),[8] are amorphous.

Experimental Section

Hexafluoroisobutylene was obtained from Daikin Corp. and used without further purification. NMR spectra were obtained in $CDCl_3$ solution: ^1H (TMS standard, ppm) 6.33; ^{13}C (TMS standard, ppm) 130.3 (C_α, $J_{C-F} = 33.5$ Hz), 127.5 (C_β, $J_{C-F} = 4.8$ Hz), 120.4 (CF_3, $J_{C-F} = 273$ Hz); ^{19}F (C_6F_6 standard, ppm), −66.6. Vinyl acetate (Aldrich) was purified by fractional distillation. Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from ether. Vazo-33 (2,2-azobis(2,4-dimethyl-4-methoxyvaleronitrile)) was obtained from Du Pont and was used as received. Trichloroacetyl peroxide (TCAP) was prepared in situ by a known procedure.[9] Elemental analysis was performed by Schwarzkopf Lab.

The polymerizations of HFIB with VA were carried out under autogeneous pressure in glass tubes equipped with Teflon needle valves. Monomers were quantitatively introduced by vacuum transfer. The homogeneous polymerizations were carried out in bulk or in 1,1,3-trichlorotrifluoroethane solution at 30 and 0 °C. AIBN or Vazo-33 was used as initiator for polymerization at 30 °C while TCAP was used at 0 °C. The polymerization reaction was quenched by rapid cooling in liquid nitrogen. The polymer was collected and purified by precipitating it three times from a methylene chloride solution into methanol.

Copolymers of HFIB with vinyl alcohol (VOH) were obtained by hydrolysis of the HFIB–VA copolymer in THF solution under normal conditions (KOH, 60 °C/5 h). No residual acetoxy group was detected by NMR.

NMR experiments were carried out on a Varian XL-400 spectrometer, at frequencies of 400, 376.3, and 100 MHz for proton, fluorine, and carbon-13, respectively. DSC measurements were performed on a Du Pont 9900 instrument. X-ray diffraction patterns were obtained in the parafocus mode with Cu Kα radiation on a Philips diffractometer. Molecular weights were determined by light scattering in THF solution.

Results

Copolymer Composition. The electron deficiency of the HFIB double bond can be readily visualized from the ^{13}C NMR data of the monomer.[10,11] From the large chemical shift difference of the β-carbons of HFIB and VA (127.5 and 96.2 ppm, respectively), one may expect a preferred cross-propagation of these two monomers since the β-carbon chemical shift difference between comonomers has been suggested as a measure of alternation.[12–14] In the present copolymerization, as long as the mole fraction of VA in monomer load does not exceed 0.7, the resulted copolymer composition is always very close to 1:1. This is clearly shown in the monomer feed versus copolymer composition relationship of Figure 1 and Table