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Computer-Assisted Resolution of Phosphorescence Spectra from Solid Films of Poly(*N*-vinylcarbazole)

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ABSTRACT: Triplet emission spectra were recorded for solid film samples of poly(*N*-vinylcarbazole) prepared by free radical polymerization at temperatures ranging from 2 to 160 °C. The low-temperature polymerizations were initiated photochemically. The phosphorescence spectra could be resolved by computer methods into three overlapping Gaussian components exhibiting peak maxima at 477 (±3), 507 (±3), and 542 nm (±3 nm). Inconsistent results were obtained from attempted two-component fits and it is concluded that there are at least three emitting triplet excimeric species present. The 477-nm band is believed to be associated with the half-eclipsed excimer while that at 507 nm is assigned to the normal sandwich excimer. The 542-nm band is thought to be due to an extended excimer consisting of three properly oriented chromophore groups. Relative oscillator strengths of these three emissions were determined for all polymer samples. Certain regularities in these values were found, depending upon polymerization conditions and mode of sample treatment.

Introduction

Poly(*N*-vinylcarbazole) (PVCA) when subjected to photoexcitation produces a rich array of photophysical phenomena, including photoconductivity, fluorescence, excimer fluorescence, phosphorescence, delayed fluorescence, excimer phosphorescence, and delayed excimer fluorescence. The latter four emissions originate from the triplet state of PVCA and are the primary focus of the present work.

In point of fact, the scope of the present study can be even more narrowly defined since it is only pure solid films of PVCA that will be considered here. It has been pointed out in earlier work[1] that the triplet luminescence of PVCA is entirely excimeric in character when it is solid films that are being photoexcited. On the other hand, no emission due to triplet excimers has been reported from frozen solutions of PVCA. Thus, a restriction to triplet luminescence from solid films is de facto a restriction to triplet excimer emission.

The modes of polymerization and sample preparation studied in this work are associated with effects that are essentially thermal in character. These may be characterized as (a) effects of polymerization temperature and (b) effects of thermal treatment of sample films. We should hasten to remark, at this point, that the polymerization temperature can indeed influence many characteristics of the resulting polymer, not the least of which is average molecular weight. The influence of average molecular weight on the triplet emission spectra of PVCA and other polymers has already been thoroughly explored by others,[2,3] however, and, apart from recognizing its influence on relative emission intensities of delayed fluorescence and phosphorescence, it is not of primary interest here.

A concern over the effects that polymerization temperature may have upon triplet luminescence characteristics of PVCA is prompted by two earlier observations. It had been noted by Houben and co-workers[4] that PVCA prepared by cationic polymerization at −78 °C emitted a relatively larger proportion of its excimer fluorescence at a wavelength corresponding to the sandwich type of excimer rather than the higher energy half-eclipsed excimer. This latter excimeric species incidentally has been shown to arise from a half-overlapped orientation of carbazolyl

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units such that only one of the aromatic rings of each chromophore is involved.[5,6] Houben et al.[4] as well as Rippen and Klöpffer[7] reasoned that the cationic polymerization led to a larger fraction of stereoregular sequences in the resulting polymer than did conventional free radical polymerization. It was later shown that solid films of cationically polymerized PVCA also produced phosphorescence spectra having a center of gravity shifted noticeably to the red compared with those of free radically polymerized material.[8]

These important observations demonstrate the significant potential of luminescence spectroscopy applied to questions of polymer microstructure and raised the question of whether or not free radical polymerization carried out at various temperatures could also lead to polymers having discernibly distinct spectral features. As a matter of fact, very definite shifts of phosphorescence emission spectra with varying polymerization temperature are observed as will be described in detail below.

The other aspect of sample history that will be explored here involves the preparation of sample films. In earlier work on the kinetics of the phosphorescence decay from PVCA films,[9] it was found that two characteristic decay times of 1.5 and 7.5 s could be observed. It was noted, however, that the portion of the total decay event associated with the long-time component was extended by heating the solution-cast film samples under vacuum at 100 °C. A vacuum treatment was chosen simply to avoid the possibility of oxidative degradation and to remove final traces of solvent. The implication of these results was that the vacuum treatment had given rise to a redistribution of the relative accessibility of excimeric components. Although it is reasonable to anticipate that such a redistribution would result in spectral shifts as well as the above-mentioned alterations of decay kinetics, no systematic attempt has been made to observe and analyze such shifts. Of course the mechanistic possibilities that could give rise to these phenomena are yet to be explored as well.

In this paper, we document the alterations of triplet luminescence that occur when various modes of sample treatment are carried out upon a wide variety of PVCA samples. With the help of computer-assisted spectral resolution it is possible to reach a number of important conclusions about the mechanisms of chain segmental alterations observed. Conversely, it becomes increasing evident that luminescence spectroscopy can be an important aid in the characterization of polymer structure and conformation.

Experimental Section

The polymer samples prepared in this work were all synthesized by free radical polymerizations using azobis(isobutyronitile) (AIBN) as the initiator. Both AIBN and *N*-vinylcarbazole were purified by multiple recrystallization from ethanol. The reaction solutions were prepared by using benzene as a solvent and, in each case, the solutions were degassed by three freeze–pump–thaw cycles followed by sealing off under vacuum.

The polymerizations at 60 °C and higher temperatures were carried out in a thermostated oven with temperature control at ±2 °C. The polymerizations at 25 and 2 °C were carried out in a thermostated water bath with temperature control at ±0.1 °C. These two low-temperature polymerizations were initiated by photodissociation of AIBN using a 100-W mercury arc lamp. The polymerization at 25 °C was completely homogeneous but at 2 °C the polymer partially precipitated from solution as it was formed.

The polymers were purified in the usual way by multiple reprecipitation, using benzene as solvent and methanol as nonsolvent. The extra precaution of carrying out these reprecipitations under a nitrogen atmosphere is a glovebox led to results no different from those found by working in the air so the glovebox procedure was eventually discontinued.

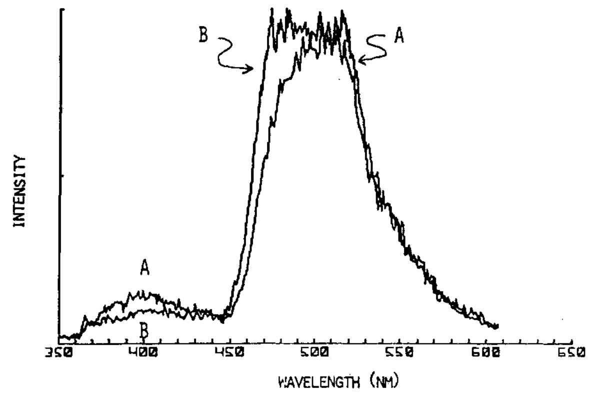

Figure 1. Triplet luminescence spectra recorded at 77 K for PVCA samples polymerized at (A) 25 °C and (B) 160 °C.

Benzene was purified before use by shaking with concentrated H_2SO_4, dilute NaOH, and distilled water followed by drying over anhydrous Na_2SO_4 and distilling. Methanol was refluxed over and distilled from $CuSO_4$, Ca shavings, and $AgNO_3$ prior to use.

Film samples were cast from benzene solutions either on optically flat quartz disks or on quartz rods. The disk samples were allowed to dry slowly in covered petri dishes inside a desiccator. The rods were spun at 120 rpm while the polymer solution was added slowly by dropwise application from a pipet. Spinning was continued until a clear, dry film was obtained. In many cases, additional treatment of these films was carried out and these will be described in detail below at the appropriate places.

Delayed luminescence spectra were recorded digitally with a Nicolet Model 1072 signal averager. Typically, four spectra were run and averaged for each sample. The excitation source was a 1000-W mercury–xenon lamp interrupted by a mechanical chopper driven by a synchronous motor. The emission signal was also interrupted by a mechanical chopper phased to admit only luminescence and no excitation light into the monochromator–detector system. A time delay of 50 ms was typically used between the excitation pulse and the measurement of the luminescence signal. The data were transfered to a CDC Cyber C730 computer for subsequent graphical display and for analytical procedures described in detail below. Additional details concerning the spectroscopic equipment are contained in several earlier papers from this laboratory.[10]

Results and Discussion

The major influence of polymerization temperature upon triplet luminescence spectra is illustrated in Figure 1. Here the effect of temperature extremes of 25 vs. 160 °C are compared. In both cases, a definite delayed excimer fluorescence emission is observed between 370 and 440 nm. The excimer phosphorescence band is clearly observed between 450 and 580 nm and, in addition, a definite shift of the center of gravity of the phosphorescence bands for these two samples is observed.

In Figure 2 are shown the results of applying our band-fitting program to these spectra.[11] The major assumptions used in this analysis are that the band shapes are Gaussian and that there are three emitting species. Since both of these assumptions are key components of the subsequent discussion, let us examine them carefully before proceeding further.

The assumption of a Gaussion band shape is based primarily upon available evidence from single-component excimer luminescence. In PVCA itself the fluorescence from the high-energy, or so-called second excimer, overlaps with monomeric fluorescence so it is difficult to assign its band shape. The normal excimer at 420 nm is somewhat more isolated and its long-wavelength side certainly appears Gaussian.[12] The phosphorescence spectrum of PVCA at 77 K is, of course, an overlapped multiple

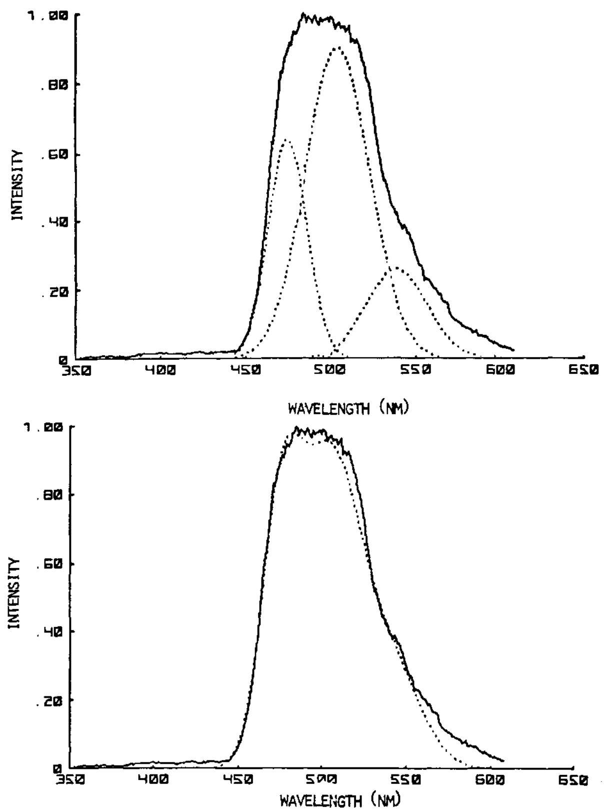

Figure 2. Results of applying the band-fitting program assuming three Gaussian components to a typical PVCA phosphorescence spectrum. Dotted lines are calculated results with individual components on upper graph and the summation curve on lower graph.

emission but at ambient temperature it appears as a single Gaussian component. Many excimeric fluorescence emission spectra from polymers are to be found in the well-known paper of Vala, Haebig, and Rice, including those for polystyrene and poly(vinylnaphthalene).[13] Again, the band shapes are best described as Gaussian. In addition, the excimer phosphorescence of poly(1-vinylnaphthalene), which appears to be a two-component system at 77 K, emerges as a single very definite Gaussian component at 180 K.[14] Finally, our band-fitting programs include Lorentzians as well as Gaussians and a number of attempts to fit observed PVCA phosphorescence spectra were made by using three Lorentzian components. No satisfactory results could be obtained with Lorentzian components; however, as the results of Figure 2 show, an excellent fit is obtained with Gaussians.

The second assumption that three triplet excimer components are required has gradually evolved from attempts to obtain consistent results from a minimum number of component Gaussians. It was initially supposed that two components would suffice, corresponding to the two known singlet excimer species of PVCA. An example of an attempt at a two-component fit is presented in Figure 3. The clear superiority of the three-component fit is evident by a visual inspection of Figures 2 and 3 and also by the significantly better standard deviation calculated for the three-component case. Although this result is satisfying, it is not by itself sufficiently compelling to claim that our assumption is justified. The reason for this is that, in general, one expects to be able to fit any emission envelope with a sufficiently large number of components. Thus, to observe that three is better than two is hardly surprising. We therefore turn to a second criterion for choosing three components, which is best demonstrated by referring to Table I.

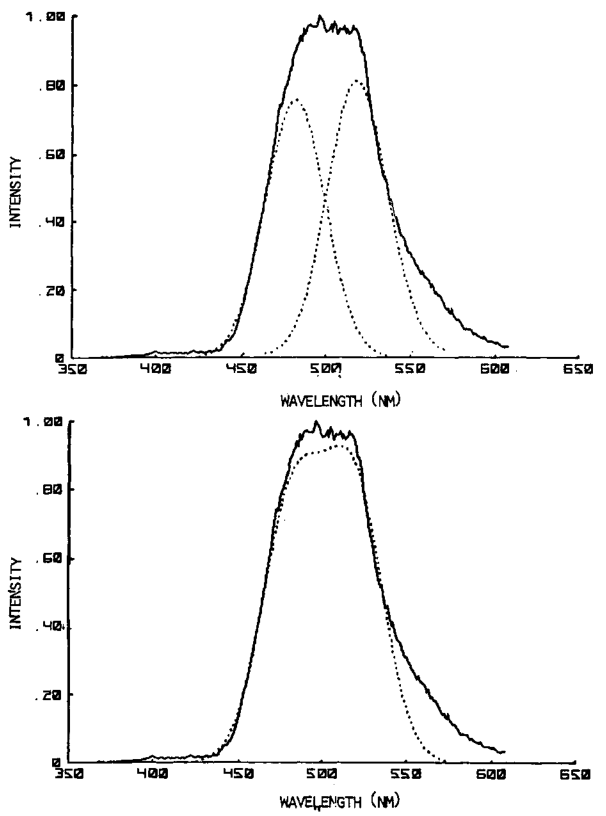

Figure 3. Results of an attempted fit to a PVCA phosphorescence spectrum using two Gaussian components. Dotted lines are calculated results with individual components on upper graph and the summation curve on lower graph.

Table I
Best Fit Values of λ_{max} (nm) and Half-Bandwidths at 1/e from the Peak Obtained from Three-Component Gaussian Band Fitting of PVCA Films Polymerized at Various Temperatures[a]

polymn temp, °C	band centers, nm			half-bandwidths, nm		
	1	2	3	W_1	W_2	W_3
2	473	500	541	10.9	31.1	37.5
25	482	513	545	21.0	26.5	30.8
65	474	505	537	18.4	24.7	35.0
100	480	509	548	17.9	22.4	25.0
125	476	507	541	17.7	25.2	35.0
160	476	507	538	17.6	23.0	35.0
	477 ± 3[b]	507 ± 3[b]	542 ± 3[b]	17.6[b]	23.0[b]	35.0[b]

[a] Film samples were cast from benzene solution and heated at 100 °C overnight in a vacuum oven. [b] Average values.

In this table are listed best fit values for the λ_{max} of each component as well as the half-width of the band at 1/e from the peak. It may be mentioned, at this point, that the band-fitting program requires initial estimates of the band center, the half-bandwidth, and the peak amplitude for each component. Iterative calculations are then performed, up to a maximum of 15, to seek a minimum standard deviation. The calculation terminates at a standard deviation of 0.01 or 15 iterations, whichever comes first. Each of the PVCA sample films listed in Table I was prepared by casting from a benzene solution followed by overnight heating at 100 °C in a vacuum oven. The results that deserve particular attention are the best fit band centers found for these samples. The average values are 477 ± 3, 507 ± 3, and 542 ± 3 nm. Thus, there is very little random error associated with these values and no discernible tendency for the best fit band centers to shift as the center of gravity of the entire band envelope

Table II
Best Fit Values of Relative Oscillator Strengths and Peak Amplitudes for Three-Component Gaussian Band Fitting of the Phosphorescence Emission of PVCA Films Polymerized at Various Temperatures[a]

polymn temp, °C	rel oscillator strengths, %			peak amplitude of emission components		
	A_1	A_2	A_3	P_1	P_2	P_3
2	24	66	10	0.47	0.96	0.20
25	40	39	21	0.70	0.76	0.28
65	24	52	24	0.67	0.79	0.30
100	36	46	18	0.73	0.85	0.37
125	39	43	18	0.74	0.77	0.34
160	38	40	22	0.81	0.75	0.31

[a] Film samples were cast from benzene solution and heated at 100 °C overnight in a vacuum oven.

changes. This is, of course, the expected behavior if the best fit band centers correspond to emission maxima of actual emitting species. Now let us contrast this result with the findings for a two-component fit. For polymers prepared at 2, 100, and 160 °C the best fit values of λ_1 were found to be 495, 483, and 479 nm, respectively, for a two-component analysis. Those for λ_2 were found to be 528, 518, and 510 nm, respectively. Clearly, these wavelengths are shifting monotonically, suggesting that they do not correspond to real emitting species. For these reasons it is concluded that the three components do, in fact, correspond to three separate excimeric species responsible for the observed phosphorescence emission.

In addition to the three-component fit obtained with this calculation, one also obtains relative oscillator strengths of the transitions involved by numerical evaluation of the integral $A_n = \int_n I(\omega)\, d\omega$ taken over the component bands, where $I(\omega)$ is the intensity of the phosphorescence emission at wavenumber ω and A_n is the relative oscillator strength of the nth component. For each sample, the signal corresponding to maximum emission intensity is set equal to unity. In Table II, a summary is given of the relative oscillator strengths A_1, A_2, and A_3 corresponding to the band centers 477, 507, and 542 nm. The best fit peak amplitudes are also presented in this table. Since the sums $A_1 + A_2 + A_3$ vary somewhat from sample to sample, they are presented in this table as percentages so that direct comparisons between samples can be made. The film samples of Tables I and II were prepared by casting from benzene solution followed by heating at 100 °C in a vacuum oven overnight. By contrast, the results presented in Table III refer to film samples that were cast from benzene solution and not treated further.

Duplicate polymerizations were carried out at 25, 100, and 160 °C. The initiator concentrations were varied in order to produce samples having varying molecular weights. No dependence of the best fit band centers or relative oscillator strengths upon molecular weight was observed.

Several trends appear in Tables I–III that should be emphasized. It is clear, of course, that the 477- and 507-nm components are, in every case, responsible for the major portion of the phosphorescence signal. In no instance does the 542-nm component account for more than 24% of the emission signal. Furthermore, in most of the film samples, the 507-nm component emerges as having the largest emission intensity. The polymer prepared at 2 °C is most remarkable in this respect in that nearly 70% phosphorescence emission arises from this 507-nm band.

Another trend may be observed by comparing relative intensities of heat-treated and untreated film samples. In general both A_1 and A_3 values are smaller for untreated films than for heat-treated ones. On the other hand, this heat treatment produces a decrease in the intensity of the A_2 component. In addition, there is a monotonic increase of the intensity of the A_2 emission between polymerization temperatures of 25 and 160 °C for untreated films; however, this trend is essentially eliminated upon heat treatment.

Table III
Best Fit Values of Relative Oscillator Strengths for Three-Component Gaussian Band Fitting of the Phosphorescence Emission of PVCA Films Polymerized at Various Temperatures[a]

polymn temp, °C	A_1	A_2	A_3
2	18	71	11
25	54	28	18
65	22	39	39
100	34	51	15
125	28	54	18
160	25	59	16

[a] Film samples were cast from benzene solution but not treated further.

Before attempting a mechanistic interpretation of these thermal effects, let us consider the assignment of particular excimeric species to the three phosphorescence emission bands observed. It is assumed in this discussion that the commonly used geometrical description of excimers in the singlet state may also be used for triplet species. No clear evidence on this point exists; however, there is also no reason to suspect that sandwich and half-eclipsed excimers might not exist in both singlet and triplet states. It seems natural to assign the 477-nm component to the half-overlapped, or staggered, excimer, which is also responsible for the 370-nm fluorescence band of PVCA.[5,6] In 2,4-dicarbazolylpentane, this particular emission most likely arises from trans–trans rotational states of the racemic material.[6] No other excimeric species which might emit at an even higher energy is known; therefore, this assignment arises by default.

A similar line of reasoning may be used for the remaining two emitting components since it is most likely that one of these components may be associated with the normal sandwich excimer. If the 543-nm component were assigned to the sandwich excimer, then it would be necessary to postulate the existence of an excimeric species intermediate in energy between the sandwich and half-overlapped species to account for the 507-nm emission, which is the strongest phosphorescent component of the band envelope. It seems much more reasonable to assign the relatively strong 507-nm emission to the sandwich excimer. This assignment then brings us to the 542-nm component.

This third component has not been isolated in fluorescence emission spectra but a third triplet species has frequently been postulated to account for various aspects of solid film phosphorescence spectra of PVCA.[7,15] Since it is clearly the rotational states of chain diads along with their stereoisomeric character (i.e., meso or *d,l*-racemic) that determines which excimeric species will be formed, it is certainly possible that neighboring diads could exist in states that would lead to three or more chromophore groups having the correct stereoregularity and the correct rotational isomerism to form extended sandwich species. Thus, it seems that the most likely source of the 543-nm phosphorescence is a triad of chromophores in which each pair is presented in a sandwich configuration. Perhaps even more extended excimer groupings exist involving four or more chromophores but, if so, they apparently do not contribute sufficiently to the total emission band to be separated from random noise.

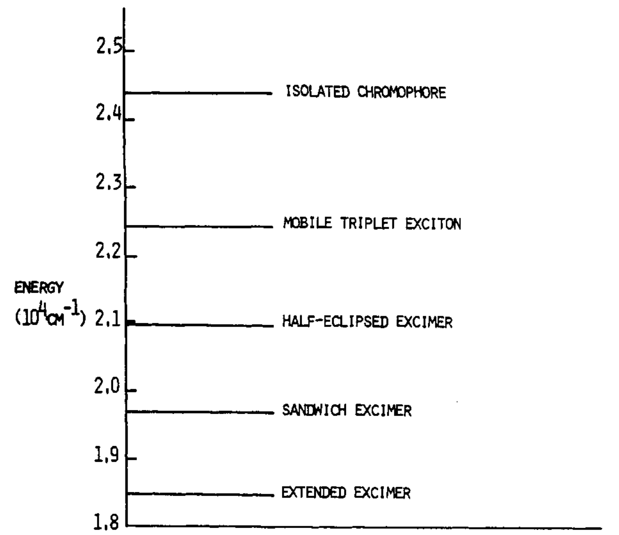

Figure 4. A suggested energy level diagram for the various triplet species thought to be present following photoexcitation of a PVCA solid film at 77 K.

Now let us finally examine other experimental results in addition to the band-fitting work for consistency with the above assignments. If one starts from the high-energy edge of the phosphorescence envelope, it is clear that the excimeric species emitting here are energetically closest to isolated chromophore groups. A suggested triplet energy level diagram is presented in Figure 4, where excimer energies are determined by their best fit values of λ_{max}. From earlier work, it has been noted that the energy level of mobile triplet excitons in PVCA is in the range 2.07×10^4 to 2.14×10^4 cm^{-1} or about 2000 cm^{-1} below that of isolated carbazolyl chromophores.[9] Although the reason for this energy mismatch is still not certain, there is the definite implication that a mobile equilibrium should exist between the half-eclipsed excimer state and the mobile exciton state since they appear to be separated by only a few hundred wavenumbers at most. Although this conclusion is consistent with energetic considerations, it is also consistent with the expectation that the half-eclipsed excimer would possess a relatively shallow potential energy surface with respect to dissociative vibrational modes. That is, the mechanical model and the energy diagram are consistent.

Phosphorescence spectra from solid PVCA films show a shift in the center of gravity to longer wavelengths with increasing temperature, which is also consistent with thermally induced dissociation of half-eclipsed excimers.[9] In addition, these spectra show a single Gaussian component at 298 K having a band center coincident with the sandwich excimer. Thus, as the sample temperature increases, one finds a decline not only in emission due to half-eclipsed excimers but also in emission due to extended excimers such that both are essentially absent at ambient temperature. The loss in emission due to the extended excimer probably does not arise from vibrationally induced dissociation to form mobile excitons. This may be inferred from the energy diagram of Figure 4, indicating an energy gap of about 3000 cm^{-1} between the extended excimer and the mobile exciton.

The various excimer states being discussed here arise from photoexcitation or mobile exciton trapping at sites in the polymer chain capable of forming the excimer upon an accompanying reorientation to the excited-state geometry. This capability is thought to involve the existence of a chain conformation that is similar to the excimer geometry. It is perhaps a temperature dependence of these ground-state conformations that results in the loss of extended excimer phosphorescence at ambient temperature. Thus, excimer species lying at energies both above and below that of the sandwich excimer are selectively eliminated with increasing temperature, but probably by way of independent mechanisms.

The data of Tables I–III show that the phosphorescence emission spectra of PVCA films depend somewhat upon the temperature of polymerization. It has been noted above that for untreated films the (Table III) intensities of the half-eclipsed excimer band decreases with increasing polymerization temperature while the intensities of the sandwich excimer show the opposite trend. The polymerization carried out at 2 °C stands as an exception to this generalization; however, the fact that the polymer precipitated from the reaction media during this particular polymerization may contribute to its singular behavior. When the films are heated at 100 °C overnight in a vacuum oven, the overriding effect is that the emission from the three components is more evenly distributed. That is, sandwich excimer emission is lost while that of the half-eclipsed and extended excimers increases somewhat.

Studies of the model compound 2,4-dicarbazolylpentane (DCP)[6] help in the intrepretation of the present results. In solution it appears that the lowest energy pathway to the half-eclipsed excimer involves the trans–trans conformation of a *d,l*-racemic diad whereas the sandwich excimer is associated with a trans–trans conformation of a meso diad. If we adopt this also as a reasonable view of the solid polymer, then it would be concluded that 477- and 507-nm emissions respectively reflect relative populations of trans–trans conformations of racemic and meso diads, respectively. Of course, phosphorescence efficiencies to be associated with these species are presently unknown and so we cannot take emission intensity ratios to be equivalent to population ratios. However, when these ratios change as a function of some controllable variable such as polymerization temperature, then alterations in relative populations of the species may be inferred.

With these working models in mind, the effect of the heat treatment applied to cast polymer films may be interpreted as resulting in the loss of trans–trans meso diads and a gain in trans–trans–trans meso triads as well as a gain in trans–trans racemic diads. Furthermore, an increase of polymerization temperature leads to the formation of untreated films having increasing populations of trans–trans racemic diads. It is tempting to conclude from this that the phosphorescence spectra of untreated films can be used to estimate relative populations meso vs. *d,l*-racemic diads in the polymer chain. Although this may, in fact, be true, additional corroborative data need to be gathered. The prospect that phosphorescence spectroscopy can potentially yield this sort of microstructural detail provides the impetus for additional work.

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Registry No. PVCA (homopolymer), 25067-59-8.

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Monte Carlo Calculations for Linear and Star Polymers with Intramolecular Interactions. 1. Dimensions

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ABSTRACT: A polymer model that includes a Gaussian distribution of distances between neighboring elements and a Lennard-Jones intramolecular potential to account for long-range interactions has been applied to describe the change with temperature of the linear chain dimensions with different values of the number of chain elements, *N*. The calculations have been performed by means of a Monte Carlo method. The results for the low- and high-temperature ranges have been analyzed, and the reduced temperature for which the mean quadratic radii of gyration are proportional to *N* is adopted as the unperturbed state. Monte Carlo calculations for star chains with different numbers of arms at this reduced temperature and subsequent extrapolation to the long-chain limit have allowed us to obtain values of the dimension ratio *g* in fair agreement with experimental data. The influence of finite-size effects on the validity of the different features shown by the model is explicitly discussed.

Introduction

Determining the influence of temperature on the conformational properties of a polymer chain in dilute solution has been the goal of many studies in the past.[1,2] This influence affects the balance between the intramolecular interactions of polymer segments and the interactions of these segments with the solvent. At high temperatures the long-range repulsive intramolecular interactions give rise to the excluded-volume effect, and the polymer becomes a swollen coil. At low temperatures the segments try to avoid contact with the solvent and the polymer collapses, adopting a globular form. At $T = \Theta$ (theta temperature) for a given solvent, both types of interactions are equivalent and the polymer is in its unperturbed state. The polymer collapse in the low-temperature region competes with condensation of the polymer phase so that only recent experimental studies[3-5] performed at high dilution have been able to detect the transition to the globular form.

From the theoretical macroscopic point of view, the coil–globule transition can be described through extended versions of the Flory mean field theory.[1,2] These types of approaches, together with the approximation $T \approx \Theta$ (i.e., for temperatures not too different from $T = \Theta$), lead to equations with the generic form[4]

$$\alpha^5 - \alpha^3 - \gamma^2/\alpha^3 = CN^{1/2}(1 - \Theta/T) \qquad (1)$$

where α^2 is the expansion factor of the polymer mean quadratic radius of gyration ($\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_\Theta$, i.e., the ratio between the mean quadratic radii of gyration at T and Θ). C is a numerical constant, and γ is a parameter proportional to the volume of a segment. The only change of eq 1 with respect to the well-known Flory equation is the addition of term $-\gamma^2/\alpha^3$, taking care of the contribution of three-body clusters to the free energy.

A different insight is provided by numerical results obtained from simulation calculations based on polymer models. These models include intramolecular potentials with attractive and repulsive terms so that they can mimic in a first approximation the balance of intramolecular and polymer–solvent interactions. This way the solvent structure can be excluded from the simulation procedures. Thus, McCrackin et al.[6] used a lattice model for the polymer in which repulsions between the chain elements were represented by a hard-sphere potential and attractions between elements in neighboring sites were described by a parametric constant. More recently, Baumgärtner[7] has used an off-lattice polymer model composed by beads jointed by randomly oriented rigid bonds, the beads interacting through a Lennard-Jones (LJ) potential. In this model each bond is understood to represent a segment of a real chain so that each segment consists of an average number of skeletal atoms. The length of the segments does not depend on temperature and is chosen to be larger than the hard-core distance of the intramolecular forces, taking into account the limited flexibility of the real polymer. The long-range attraction between the bonds resulting from the mutual interaction of polymer and solvent is taken into account by the LJ potential, whose depth measures, at least in a first approximation, the energy of the polymer–polymer intramolecular interaction relative to that of the polymer–solvent interaction. This type of relatively soft potential seems somewhat more realistic than hard-core potentials to describe interactions between units representing flexible subchains for which the real interactions between chemical groups included in the interacting theoretical beads are not simple functions of the distance between the bead centers. Also, Webman et al.[8] have studied a model that considers beads connected by springs and interacting according with a LJ potential. The latter model seems to be more realistic since the segments of a long flexible chain can be described as Gaussian subchains and a Gaussian distribution of distances is also followed in the spring–bead model. However, the mean distance between neighboring segments, *b*, is in this model temperature-dependent since LJ interactions are also considered between these segments.

These off-lattice methods, in addition to being more realistic than lattice models, also offer the possibility of varying more parameters relevant to the problem (in the

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