Triplet Emission from Poly(3,6-dibromo-*N*-vinylcarbazole): Spectra and Kinetics

Franciszek C. Starzyk[†] **and Richard D. Burkhart***

Department of Chemistry, University of Nevada—Reno, Reno, Nevada 89557.

Received June 14, 1988; Revised Manuscript Received August 19, 1988

ABSTRACT: The triplet delayed emission of poly(3,6-dibromo-*N*-vinylcarbazole) (PdBVK) in a 2-methyltetrahydrofuran (MTHF) frozen solution at 77 K was examined within the spectral and time regimes of 400–570 nm and 0.2–50 ms, respectively. The influence on optical absorption of bromine substitution into the carbazole ring (3- and 6-positions) of poly(*N*-vinylcarbazole), as well as delayed triplet emission spectra and the kinetic decays, was monitored. The phosphorescence spectra were recorded at different delay times after excitation. The phosphorescence decays were found to be essentially exponential in the wings of the phosphorescence band but showed unusual, definitely nonexponential, behavior in the range 460–475 nm, which is the range of maximum phosphorescence intensity. A resolution of the phosphorescence band into Gaussian components yielded excellent fits by using three components at delay times less than 2 ms and two components for spectra taken at longer delay times. Based upon an average of 12 different spectra recorded at various times after excitation, the calculated wavelengths at maximum intensity for these Gaussian components were found to be 448 ± 2 nm, 473 ± 4 nm, and 501 ± 8 nm. The 501-nm component is rather broad and is always the least intense of the three component bands. It is also the one that disappears at delay times longer than 2 ms after the excitation pulse. The 448-nm component may originate from independent chromophoric groups or may be a trapped species not very different in energy from the triplet state of individual chromophores. The 473-nm component presumably is associated with deeper energy trap sites, possibly excimeric in nature. The origin of the 501-nm component is uncertain but may also be associated with a trap site or with a low-energy vibronic component of the independent chromphore emission.

Introduction

The triplet photophysical properties of poly(*N*-vinylcarbazole) (PVK) have been the subject of many investigations. The influence of structural modifications of PVK on its photophysical properties has also been a matter of enhanced interest.[2–4] Among other structural modifications, the substitution of bromine atoms onto carbazole aromatic rings was shown to cause a change in the ionization potential of PVK[2] as well as to enhance the singlet–triplet intersystem crossing efficiency due to the heavy atom effect.[4] Also, the triplet energy migration parameters, such as the migration coefficient and the mean exciton migration length, were reported as being substitution sensitive.[1d] The enhanced thermal stability caused by the mono- and disubstitution of halogens in 3- or 3- and 6-positions has also been reported.[5]

Yokoyama and coworkers[4] originally reported the phosphorescence spectrum of poly(3,6-dibromo-*N*-vinylcarbazole) (PdBVK) in rigid solution. They attributed the lack of any emission from solution at room temperature to efficient singlet–triplet intersystem crossing enhanced by the heavy atom effect due to the presence of bromine. The delayed emission of PdBVK showed a single broad band with a maximum around 459 nm. This structureless emission band in rigid solution was interpreted as being due to excimer phosphorescence. The possibility of triplet exciton migration along the polymeric chains was considered as well as exciton trapping at excimer sites, where two neighboring chromophores are able to form triplet excimers. The lifetime of the phosphorescence was reported to be about 32 ms monitored at a wavelength of 459 nm. No time-resolved spectra were reported for this polymer.

These observations of triplet photophysical properties are unique among vinyl aromatic polymers. It is rare to encounter an excimeric type of phosphorescence from dilute rigid solutions of these polymers although such phenomena are common for solid films. These observations made by Yokoyama and co-workers[4] seemed, therefore, to warrant a more detailed investigation using analyses of luminescence decays as well as time-resolved spectroscopy. Accordingly, this paper is devoted to a more detailed investigation of the triplet photophysical properties of PdBVK in rigid solutions at 77 K. Some unusual properties of both kinetic decays and time-resolved spectra indicate that the triplet state photophysics is more varied and more complex than originally might have been supposed.

Experimental Section

Origin and Treatment of Chemicals. The polymer used in this work is the same as that employed in the experiments of ref 2. Polymerization of the monomer (5 g) was performed at 70 °C in benzene solution (50 mL) for 8 h in the presence of azobis(isobutyronitrile) (0.01 g) as the initiator. The polymer was precipitated by adding methanol and after washing three times with methanol it was repeatedly dissolved in benzene and reprecipitated from methanol. It was then dried in a vacuum oven at 60 °C. The molecular weight, determined by polymer solution viscosity, was 30 000.

For these photophysical measurements the polymer was additionally purified by passing it through a silica-gel column. A 20-cm-long column was used and purified THF was the mobile phase. After fractionation the polymer was reprecipitated from the THF by using methanol. It was then dried once more under vacuum.

Solutions of the polymer were prepared by dissolving it in 2-methyltetrahydrofuran (MTHF) to achieve 5×10^{-3} M concentrations of chromophore groups. The MTHF solvent used was also previously purified by passing it through an activated alumina column followed by distillation in the prescence of $LiAlH_4$.

Instrumentation. Absorption spectra of the PVK and PdBVK solutions were taken with a Cary 14 spectrophotometer. The instrumentation used for photophysical measurements has been described in earlier publications from this laboratory.[6] The main features of this system are the following. The excitation source used was a Tachisto Model 401 XR XeCl excimer laser. This laser produces 308-nm light in pulses that have a time duration of about 20 ns. The laser light, after passing through a 308-nm filter, intersected the sample solution cooled in a liquid nitrogen bath. The sample emission was focused by a quartz lens onto the input slit of the monochromator. The light at the exit slit was detected by using a Thorn-EMI 9789B photomultiplier. The current, proportional to the emission intensity, was preamplified and

---

[†] On leave from the Institute of Physics, Technical University of Krakow, Krakow, Poland.

0024-9297/89/2222-0782$01.50/0 © 1989 American Chemical Society

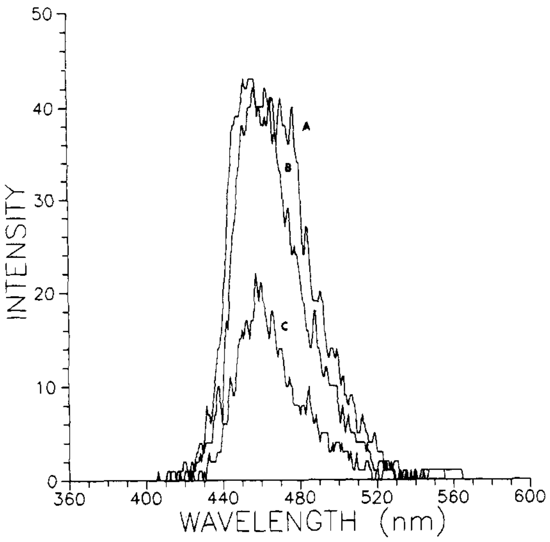

Figure 1. Delayed triplet emission from PdBVK in MTHF at 77 K. Delay times are (A) 5, (B) 10, and (C) 20 ms.

Table I
Major Features of the Absorption Spectra of PVK and PdBVK Solutions in MTHF at Room Temperature

sample	absorptn edge, nm	main peak positions, nm			
PVK	360	343	331	293	261
PdBVK	380	359	345	303	270

directed to the Nicolet 12/70 signal averager.

Experimental Results

In Table I the main features of the absorption spectra of PVK and PdBVK solutions are collected.

The bromine substituents at the 3- and 6-positions of the carbazole group evidently cause a red shift of the whole absorption spectrum of PdBVK relative to that of PVK. Since the electronic transition has significant charge-transfer character, typical of other carbazole chromophores,[7] the existence of electron-withdrawing groups in the aromatic rings have the expected effect of lowering the energy required for the transition. Similar effects have been observed by Harvey and co-workers[8] as a result of N-atom substitution into the carbazole chromophore. The energy associated with this red shift has an average value of 1231 cm^{-1} as calculated from the four main peak positions.

In Figure 1 time-resolved delayed emission from PdBVK in MTHF solution at 77 K is shown. The emission was monitored at delay times of 5, 10, and 20 ms within the spectral range from 400 to 570 nm. A relatively high-frequency electronic filtration of 10 MHz was used to avoid accidental smoothing due to inertia of the electronic response. The triplet emission for the relatively long delay times used in this study is weak and noisy. The emission maximum is near 465 nm but cannot be defined sharply especially for a delay time of 5 ms where a very broad flat maximum was observed. It should be noted that some fine structural features of these phosphorescence spectra seem to be reproducible. Any attempts to determine whether these features have physical meaning would be more

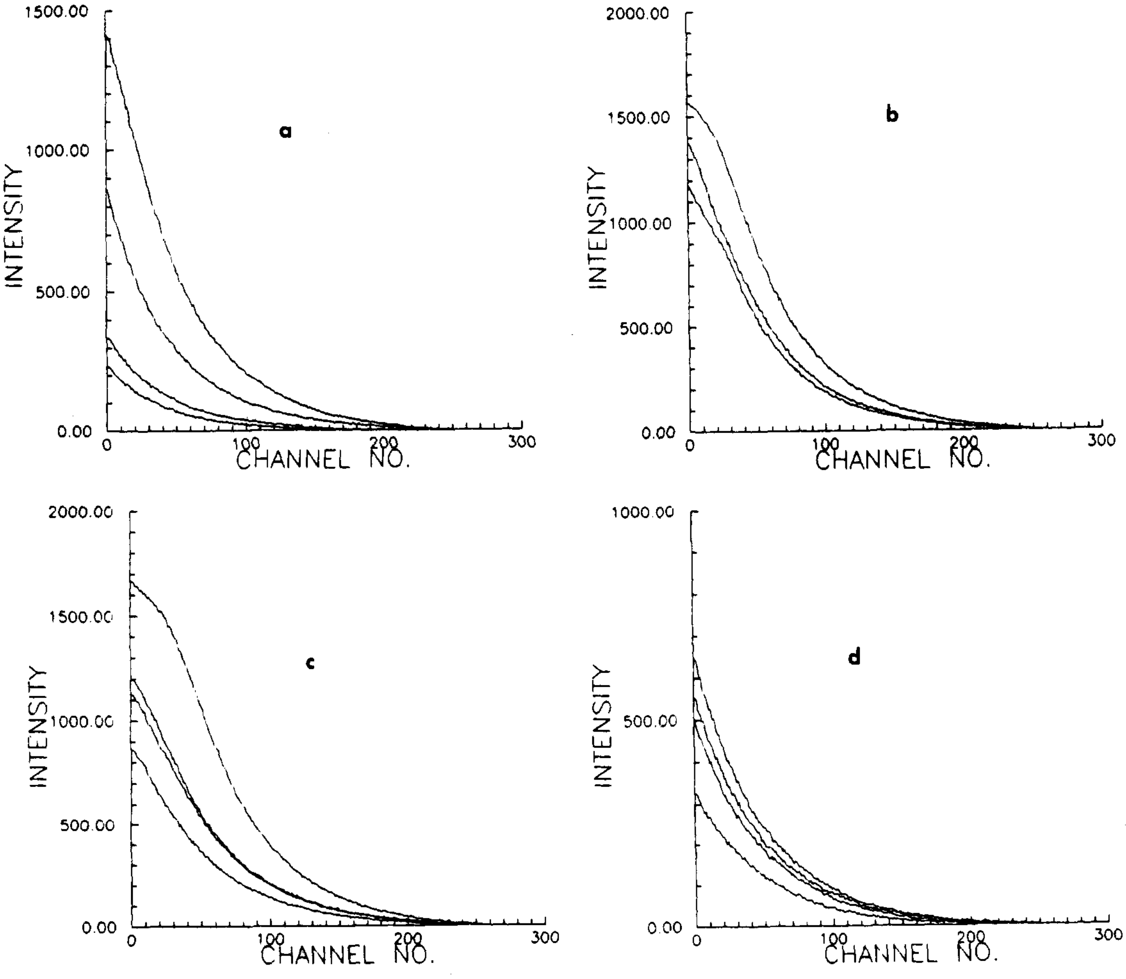

Figure 2. Decay curves for triplet emission from MTHF solution at 77 K: (a) (from bottom to top) 435, 440, 445, and 456 nm; (b) (from bottom to top) 450, 455, and 465 nm; (c) (from top to bottom) 470, 475, 480, and 485 nm; (d) (from top to bottom) 490, 495, 500, and 505 nm.

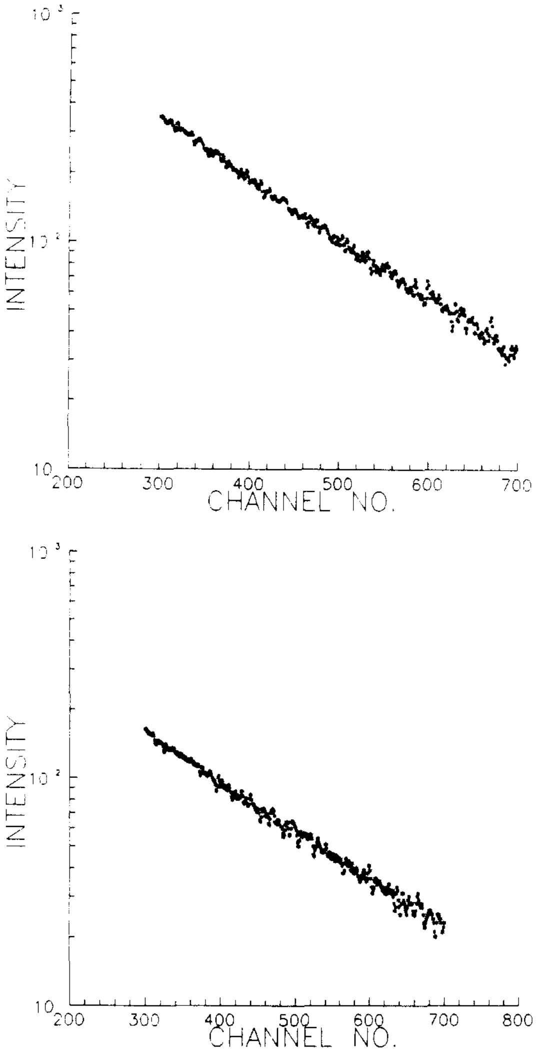

Figure 3. Semilogarithmic plot of triplet emission intensity versus time for PdBVK in MTHF at 77 K: (A, top) 450 nm, 30-ms delay; (B, bottom) 460 nm, 40-ms delay.

fruitfully investigated by using lower temperatures in the liquid helium range.

In Figure 2 the kinetic decays of triplet emission of PdBVK solution in MTHF within the range 435–505 nm are presented. The character of these decay curves depends on the wavelength used for observation. Within the range 435–450 nm, that is on the short wavelength side of the emission band, decays have an exponential-like character. In the range from 450 nm to about 475 nm a distinctly nonexponential behavior was observed. This is the region of maximum emission. Especially the curves for 460, 470, and 475 nm indicate a period of rate acceleration prior to the onset of the more normal appearing exponential decay. The long-wavelength side of the spectrum (485–505 nm) again shows the more normal exponential-like behavior. The mean lifetime was calculated for each decay by using an exponential fit program. For decays in the spectral range 460–480 nm, only points for times greater than 40 ms were used in the calculations in order to avoid the acceleration region. Thus, for the exponential-like parts of these decays the calculated value of the triplet lifetimes between 450 and 505 nm were all in the range 44.0–46.0 ms.

In order to observe the decay behavior at longer times, we recorded decays for 450 and 460 nm with delays of 30 and 40 ms, respectively. In Figure 3 these decays are shown on a semilogarithmic scale. The lifetime calculated for case (a) is 46.3 ms and the one for (b) equals 58.7 ms.

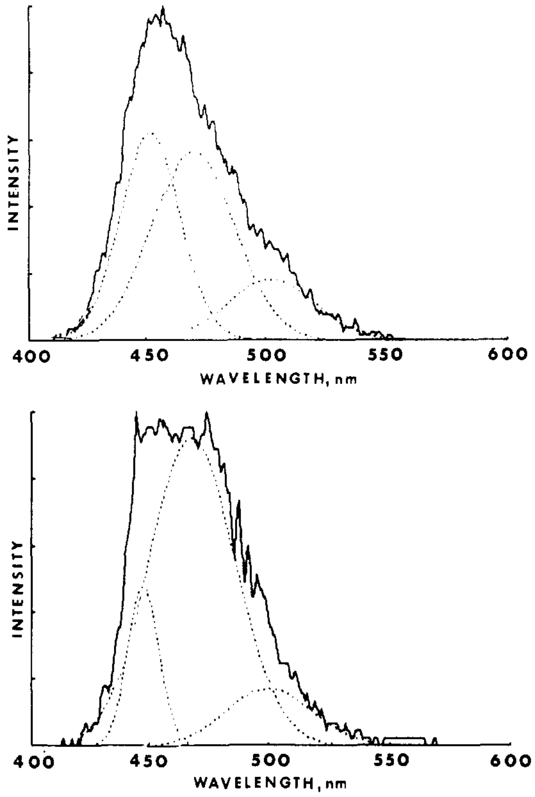

Figure 4. Gaussian components (dotted lines) yielding the best fit to indicated experimental spectra (solid lines). Upper spectrum was recorded 0.2 ms after excitation and lower at 2 ms.

Evidently the lifetimes determined near the band center deviate somewhat from single-exponential behavior. On the other hand, an exponential fit to the decay data at the hight-energy extreme of the phosphorescence band at 435 nm yielded a significantly faster lifetime value of 41.5 ms.

The behavior of the kinetic decays in the region of 460–470 nm indicates very clearly that there is more than one species responsible for the emission in this spectral range. It was decided, therefore, to use a spectral deconvolution technique as a means of estimating the number and position of the spectral bands underlying the phosphorescence envelope. The methods used have been discussed in previous work from this laboratory.

We have available both Lorentzian and Gaussian programs which can fit up to six component species. A detailed description of these deconvolution procedures and their application to solid-state phosphorescence of PVK may be found in ref 1e. Attempted fitting using Lorentzians was not successful but it was eventually found that very good fitting to experimental spectra recorded at delay times of 2 ms or less could be achieved by using three Gaussian components. At longer delay times only two components were required for satisfactory fitting. Figure 4 gives the results of the deconvolution for spectra recorded at 0.2 and 2.0 ms after the excitation pulse. A total of 12 different spectra were analyzed in this way and the average values for the band centers were found to be 448 ± 2 nm, 473 ± 4 nm, and 501 ± 8 nm. The maximum intensity of the 501-nm component was always the weakest of the three and this accounts for the relatively greater uncertainty in its position. It was also this band which disappears first at longer times after the excitation pulse thus requiring two rather than three components for an acceptable fit. It is noteworthy that the relative importance of the central broad band increases with increasing delay time at the expense of the higher energy band. It will also be noted that the width of the high-energy band appears to decrease at the longer delay time. Whether or not this is an artifact of the fitting program or a real effect is unknown. In a case of inhomogeneous broadening with an initial Gaussian distribution of states, the band may become narrower with time as triplet states seek environments of lower energy.

Discussion

The optical absorption spectrum of PdBVK indicates that the main peak positions are red-shifted relative to PVK by 1231 cm^{-1}. In addition, the molar absorptivity of each band is lower in the case of PdBVK relative to PVK. The influence of substituents at the nitrogen atom and in the rings of carbazole indicates that charge transfer from nitrogen to the aromatic rings accompanies the formation of S_1. The electron-withdrawing effect of the two Br atoms in the aromatic rings facilitates this charge-transfer process and lowers the energy required to bring it about. Therefore, the red shift observed for PdBVK is expected and is consistent with earlier interpretations of the nature of these electronic transitions.

The high-energy side of the triplet emission spectrum of PdBVK is also red-shifted with respect to that of PVK. A major question which needs to be considered, therefore, involves the identity of the species responsible for this emission. Johnson has found that the lowest triplet state of N-substituted carbazoles is predominantly polarized out of the molecular plane.[9] Indeed, it has been observed that the substitution of a strong electron-withdrawing group at the carbazole nitrogen has a negligible effect upon the phosphorescence spectrum of these species.[3] It may be noted that Yokoyama and co-workers[4] recorded the phosphorescence spectrum of 3,6-dibromo-9-ethylcarbazole in glassy MTHF at 77 K and placed its origin at 417 nm.

An interpretation of the phosphorescence spectrum of PdBVK is further complicated by two additional considerations. First, it is clear from deconvoluted spectra and from the decay kinetics that more than one species is emitting under this band envelope. In addition, it seems clear that the central component is undergoing simultaneous formation and decay at times less than about 100 ms. That is, the early time characteristic of the emission which indicates an acceleration is most likely due to competition between energy transfer to this species and its first-order relaxation to the ground state. It therefore seems likely that this central component, positioned at 473 nm, represents emission from an energy trap. The emission at 501 nm is probably also from an energy trap but, at the smallest delay times used here, no inflection in its kinetic decay is observed. Therefore it must be formed by a faster energy-transfer process than is the 473-nm component or else it arises by intersystem crossing from a trapped singlet state.

The high-energy component of this emission band centered at 448 nm exhibits lifetime characteristics which suggest that it may be the donor species involved in the energy-transfer process. That is, its emission is multiexponential with a fast early component and a slower long-time component. It is suggested, therefore, that the 448-nm band represents phosphorescence from individual PdBVK chromophores. A necessary corollary of this conclusion is that the triplet state of the dibromo chromophore when bonded to the polymer chain backbone undergoes a 30-nm red shift relative to its monomeric analogue. This sort of red shift for a polymer-bound chromophore relative to the monomeric analogue is commonly observed,[10] but such a large shift is certainly unusual. Another possibility is that the 448-nm component is also a trapped species but one which is in equilibrium with mobile triplet excitons. The present exprimental results do not allow us to distinguish between these two possibilities.

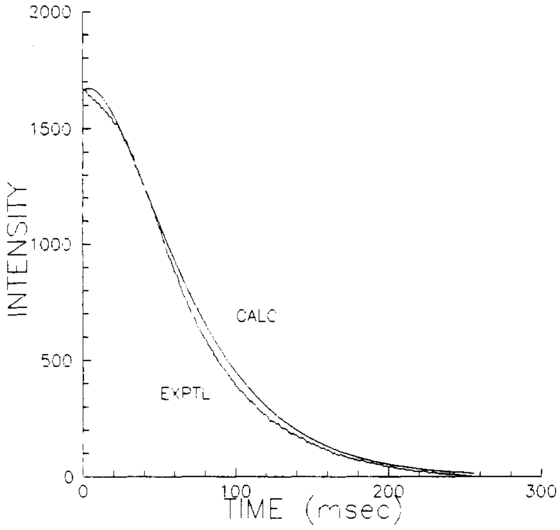

Figure 5. Experimental decay curve recorded at 470 nm compared with a calculated curve obtained assuming the major emitting species is also acting as an energy acceptor.

In order to discuss these processes more quantitatively, let us symbolize a mobile triplet exciton by T_m and the 448- and 473-nm triplet components by T_1 and T_2, respectively. Assuming T_m and T_1 are connected by a rapid mobile equilibrium, one may write

$$T_1 \rightleftarrows T_m \tag{1}$$

$$T_m + {}^1E_0 \rightarrow {}^1M_0 + T_2 \tag{2}$$

$$T_1 \rightarrow {}^1M_0 + h\nu \text{ (448 nm)/heat} \tag{3}$$

$$T_2 \rightarrow {}^1M_0 + h\nu \text{ (473 nm)/heat} \tag{4}$$

where ${}^1E_0$ represents a pair of strongly interacting ground-state chromophores capable of forming T_2 upon excitation and ${}^1M_0$ is the ground state for individual chromophores.

The time dependence of T_2 may be easily calculated by assuming the ${}^1E_0$ concentration remains essentially constant and assuming the reverse of step 1 is much faster than step two. In this case one finds

$$T_2(t) = \{[k_{e2}KT_1(0)]/(k_3 - k_4)\}[\exp(-k_4t) - \exp(-k_3t)] \tag{5}$$

where $K = k_1/k_{-1}$, $k_2{}^1E_0 = k_{e2}$, and the symbols for each of these species are meant to represent their molar concentrations. An attempt was made to use eq 5 to reproduce an experimentally determined decay. The one chosen is the uppermost curve in Figure 2c. In Figure 5 is displayed the resulting fit, assuming $k_4 = 26$ s^{-1}, $k_3 = 28$ s^{-1}, and the emission at that wavelength consists of 60% from T_2 and 40% from T_1. These best-fit rate constants are somewhat larger than would have been predicted by using a forced exponential fit to the tails of the luminescence decays (22 s^{-1}). On the other hand, they are in better agreement with a lifetime of 32 ms found by Yokoyama and co-workers.[4] In any event, considering the simplifying assumptions used in the calculations, the agreement may be deemed satisfactory.

All of the photophysical events observed in this study have been interpreted in terms of the conventional concepts of excited electronic states of the chromophores involved. At the high-energy densities reached by laser excitation and in view of the large local chromophore concentrations in the polymer coil, it is possible that upper electronic states or even ionized states may be of importance in the overall process of relaxation back to the ground state. Although no compelling evidence for the formation of charged species has been encountered in this work, it is suggested as a subject for future study especially in view of the recent interpretation of the mechanism of delayed fluorescence production in PVK subjected to laser excitation.[11]

Acknowledgment. This work was supported by a grant from the U.S. Department of Energy under Grant DE-FG08-84ER45107. We are grateful to Dr. Ewa Trembacz of the Institute of Organic Chemistry and Technology, Technical University of Krakow, for the synthesis of the subject polymer. Financial support for F. C. Starzyk was from the Nevada EPSCoR program sponsored by the National Science Foundation.

Registry No. PdBVK, 27599-53-7.

References and Notes

(1) (a) Klopffer, W. *Chem. Phys.* **1981**, *57*, 75 and earlier references cited therein. (b) Kim, N. Webber, S. E. *Macromolecules* **1985**, *18*, 741. (c) Webber, S. E., Avots-Avotins, P. E. *J. Chem. Phys.* **1980**, *72*, 3773. (d) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Jpn.* **1976**, *49*, 2037. (e) Burkhart, R. D.; Dawood, I. *Macromolecules* **1986**, *19*, 447 and earlier references cited therein.

(2) Pielichowski, J.; Starzyk, F. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 623.

(3) Burkhart, R. D.; Lee, O.; Boileau, S.; Boivin, S. *Macromolecules* **1985**, *18*, 1277.

(4) Yokoyama, M.; Funaki, M.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1974**, 372.

(5) Pielichowski, J.; Chrzaszcz, R.; Starzyk, F. In *Polymeric Amines and Ammonium Salts*; Goethals, E. J., Ed.; Pergamon Press: New York, 1980; p 389.

(6) Caldwell, N. J.; Burkhart, R. D. *Macromolecules* **1986**, *19*, 1653.

(7) Mataga, N.; Torihashi, Y.; Ezumi, K. *Theor. Chim. Acta* **1964**, *2*, 158.

(8) Harvey, P. D.; Zelent, B.; Durocher, G. *Spectrosc. Int. J.* **1983**, *2*, 128.

(9) Johnson, G. E. *J. Chem. Phys.* **1974**, *78*, 1512.

(10) Klopffer, W.; Fischer, D. *J. Polym. Sci., Polym. Symp.* **1973**, *No. 40*, 43.

(11) Stolzenburg, F.; Ries, B.; Bassler, H. *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 853.

Adsorption Kinetics of Poly(ethylene oxide) at the Air/Water Interface

Bryan B. Sauer and Hyuk Yu*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received March 28, 1988; Revised Manuscript Received August 15, 1988

ABSTRACT: With the aid of surface quasi-elastic light scattering (SLS) at the air/water interface, we established that the viscoelastic parameters of poly(ethylene oxide) (PEO) films, formed either by spreading from a methylene chloride solution or by spontaneous adsorption from aqueous solution, were identical over the entire surface pressure range. This identity was taken to infer that the PEO segments anchored at the surface are in the same physical state for both spread and adsorbed films. On this basis, the time dependence of the static surface pressure of adsorbed PEO films was used to deduce the corresponding surface concentration as a function of time. The adsorption kinetics by this method were found to be diffusion limited under certain conditions, and the resulting diffusion coefficients were shown to be in accord with those obtained by quasi-elastic light scattering on the same PEO samples in dilute aqueous solutions.

Introduction

Poly(ethylene oxide) (PEO) is known to form stable spread films[1–4] at the air/water (A/W) interface. PEO is also one of few polymers that forms such films at the A/W interface yet is water soluble in all proportions. The stability of a high molecular weight polymer film arises from its cooperativity, the large amount of interfacial contacts even if the monomer segments themselves being only mildly amphiphilic, and PEO is one of such instances. It has been shown to be extremely surface active in aqueous solutions[5–7] and thus is well suited for a comparative study of *spread* and *adsorbed* films. The schematic extremes of chain conformation adopted by a polymer adsorbed to an interface from dilute solution are as follows. At one extreme, the polymer exists in a random coil conformation, as in solution, with only a few segments in contact with the interface; a case in point is poly(methacrylic acid).[8] At the other extreme, a chain adopts a flattened, two-dimensional conformation with the majority of the segments in contact with the interface, and PEO is such a case.[1,2] In reality, the chain conformation at the interface probably comprises a certain combination of the two extremes. Since the random coil conformation arises from the predominance of configurational entropy and the planar conformation from that of adsorption enthalpy, a given combination of the two extremes reflects a manifestation of interplay of the entropic and enthalpic contributions to the adsorption free energy. For most of the spread polymer films in the dilute limit of surface segment density, the chain conformation is deduced to be in a flattened, two-dimensional one, and there are many examples of this case.[9]

Surface quasi-elastic light scattering (SLS) is a useful tool to probe the mechanism of adsorption to an interface since the film rheological parameters can be determined without knowing the surface concentration of such films; these rheological parameters are obtained by characterizing the dynamics of surface capillary waves. In a previous study,[3] we compared the dynamic longitudinal elasticity of spread PEO films determined from SLS with the static Gibbs surface elasticity. The first part of this paper deals with an extension of the SLS technique to the study of the dynamic viscoelasticity of adsorbed films for which the static Gibbs elasticity is not accessible because the surface

© 1989 American Chemical Society