Houwink expression for $[\eta]$ in eq 8

$$\log M_i = ((-1.02 - \log K) + 6.52V - 0.67V^2 + 0.024V^3 - 0.29 \times 10^{-3}V^4)/(a + 1) \quad \text{(A6)}$$

and fitting the experimental M_i vs. V_i data. The weight-average and the number-average molecular weights were calculated by using the standard summations ($\bar{M}_w = \sum(M_iW_i)/\sum W_i$) and ($\bar{M}_n = \sum W_i/\sum(W_i/M_i)$). The viscosity of the ith stripe was calculated by

$$[\eta]_i = J_{i,s}/M_i \quad \text{(A7)}$$

where $J_{i,s}$ is the hydrodynamic volume determined from the polystyrene calibration. The overall viscosity of the copolymer was then calculated by

$$[\eta] = \sum W_i[\eta]_i \quad \text{(A8)}$$

and compared to the experimentally measured value.

Registry No. (MDI)-(BD)-(PTMO) (copolymer), 9018-04-6.

References and Notes

(1) Saunders, J. H.; Frisch, K. C. *Polyurethane Chemistry and Technology: Part 1. Chemistry*; Interscience: New York, 1962.
(2) Cooper, S. L.; Tobolsky, A. V. *J. Appl. Polym. Sci.* **1966**, *10*, 1837.
(3) Estes, G. M.; Cooper, S. L.; Tobolsky, A. V. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *4*, 313.
(4) Gibson, P. E.; Vallance, M. A.; Cooper, S. L. *Developments in Block Copolymers*, Goodman, I., Ed.; Elsevier, Applied Science Publishers: London, 1982.
(5) Schollenberger, C. S.; Dinbergs, K. *J. Elastoplast.* **1973**, *5*, 222.
(6) Schollenberger, C. S.; Dinbergs, K. *J. Elastoplast.* **1979**, *11*, 58.
(7) Speckhard, T. A.; Miller, J. A.; Cooper, S. L. *Macromolecules* **1986**, *19*, 1558.
(8) Rempp, P.; Benoit, H. *Rubber Chem. Technol.* **1968**, *41*, 245.
(9) Spatorico, A. L. *J. Appl. Polym. Sci.* **1974**, *18*, 1793.
(10) Speckhard, T. A. Ph.D. Thesis, University of Wisconsin—Madison, 1985.
(11) Yau, W. W.; Jones, M. E.; Ginnard, C. R.; Bly, D. D. *ACS Symp. Ser.* **1980**, *No. 138*, 91.
(12) Janca, J. *Adv. Chromatogr.* **1981**, *19*, 37.
(13) Hamielec, A. E.; Ouano, A. C. *J. Liq. Chromatogr.* **1978**, *1*, 111.
(14) Weiss, A. R.; Cohn Ginsberg, E. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 379.
(15) Morris, M. C. *J. Chromatogr.* **1971**, *55*, 203.
(16) Dobbin, C. J. B.; Rudin, A.; Tchir, M. F. *J. Appl. Polym. Sci.* **1980**, *25*, 2985.
(17) Ouano, A. C.; Kaye, W. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1151.
(18) Ouano, A. C. *J. Chromatogr.* **1976**, *118*, 303.
(19) Jordan, R. C. *J. Liq. Chromatogr.* **1980**, *3*, 439.
(20) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979.
(21) Benoit, H.; Grubisic, Z.; Rempp, P.; Decker, D.; Zilliox, J. G. *J. Chem. Phys.* **1966**, *63*, 507.
(22) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 753.
(23) Dawkins, J. V. *Br. Polym. J.* **1972**, *4*, 87.
(24) Dawkins, J. V. *Eur. Polym. J.* **1977**, *13*, 837.
(25) Samay, G.; Kubin, M.; Podesva, J. *Agnew. Makromol. Chem.* **1978**, *72*, 185.
(26) Chu, B.; Ying, Q.; Lee, D.-c.; Wu, D.-q. *Macromolecules* **1985**, *18*, 1962.
(27) Stockmayer, W. H.; Moore, L. D., Jr.; Fixman, M.; Epstein, B. N. *J. Polym. Sci.* **1955**, *16*, 517.
(28) Hwang, K. K. S.; Yang, C. Z.; Cooper, S. L. *Polym. Eng. Sci.* **1981**, *21*, 1027.
(29) Miller, J. A.; Lin, S. B.; Hwang, K. K. S.; Wu, K. S.; Gibson, P. E.; Cooper, S. L. *Macromolecules* **1985**, *18*, 32.
(30) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716.
(31) Kraemer, E. O. *Ind. Eng. Chem.* **1938**, *30*, 1200.
(32) Tirrell, M.; Lee, L. J.; Macosko, C. W. *ACS Symp. Ser.* **1978**, *No. 104*, 149.
(33) Mrkvicakova, L.; Pokorny, S. *J. Appl. Polym. Sci.* **1985**, *30*, 1211.
(34) Flory, P. J. *Principles of Polymer Chemistry*, Cornell University: Ithaca, NY, 1953.
(35) Hamielec, A. *Pure Appl. Chem.* **1982**, *54*, 293.
(36) Miller, J. A.; Speckhard, T. A.; Cooper, S. L. *Macromolecules* **1986**, *19*, 1568.
(37) Miller, J. A.; Speckhard, T. A.; Homan, J. G.; Cooper, S. L. *Polymer*, submitted.
(38) Speckhard, T. A.; Homan, J. G.; Miller, J. A.; Cooper, S. L. *Polymer*, submitted.

Photophysical and Photochemical Behavior of Poly(1-vinylpyrene). Evidence for Dual Excimer Fluorescence

R. V. Todesco,*† R. A. Basheer,‡ and Prashant V. Kamat*

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556.

Received December 10, 1985

ABSTRACT: A high molecular weight poly(1-vinylpyrene) (PVP) has been synthesized and characterized. ^{1}H NMR spectra combined with UV spectroscopy suggested a high interaction between pyrenyl groups in the polymeric environment. The ^{13}C NMR spectrum was characteristic mainly of an atactic polymer. The singlet and triplet excited-state properties of PVP have been determined in solution at room temperature and in a matrix at 77 K. Time-dependent fluorescence measurements in THF solution at room temperature revealed the existence of two excimers with emission maxima at 485 and 530 nm. We attributed a staggered and an eclipsed conformation to the high- and low-energy excimer, respectively. In a MTHF matrix at 77 K, PVP exhibited intense structured dimer emission together with fluorescence from the high-energy excimer. Transient absorption monitored upon laser pulse (337.1 nm) excitation of PVP in THF solution indicated a very low quantum yield for the formation of triplet state ($\phi_T \leq 10^{-3}$). Upon irradiation with UV light, degradation of PVP occurred with an apparent quantum yield of 1.1×10^{-5} for random scission.

Introduction

The excited-state properties of polymers containing pendant aromatic chromophores are a topic of much current interest. Excimer-forming homopolymers[1] such as polystyrene (PS), poly(vinylnaphthalene) (PVN), and poly(*N*-vinylcarbazole) (PVNCz) have been intensively investigated, and the study of the excited-state behavior of suitable model compounds[2-6] (e.g., corresponding meso and racemic 2,4-diarylpentanes and 1,1′-diaryl diethyl ethers) clearly illustrates the importance of configurational and conformational aspects in the intramolecular excimer

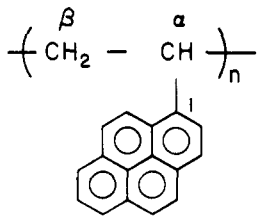
† On leave of absence from the University Centre of Limburg, Belgium.
‡ Present address: Polymer Department, General Motors Research Laboratories, Warren, MI 48090.

0024-9297/86/2219-2390$01.50/0

formation of these polychromophoric systems.

Recently spectral and time-dependent properties of the diastereoisomers of 2,4-di(1-pyrenyl)pentane (D1PP) and bis[1-(1-pyrenyl)ethyl] ether (B1PEE) have been studied,[5,6] and for both meso compounds the existence of two excimers with different decay times and spectral distributions was observed. As these compounds are models for the isotactic and heterotactic diads of poly(1-vinylpyrene) (PVP), a highly complex kinetic behavior for atactic PVP was predicted.[6] However, until now, only scarce information about the excited-state properties of PVP is available: (1) McDonald et al.[7] reported steady-state fluorescence measurements and T–T absorption spectra of PVP, but no lifetimes were determined. (2) On the other hand, Yokoyama et al.[8] obtained a single lifetime of 160 ns for the observed PVP excimer. (3) Recently excimer lifetimes of about 110 ns were reported for PVP, prepared by both electrochemical and photoelectrochemical means and by using Ziegler–Natta catalyst.[9] In the same work the occurrence of a shorter lived species was detected, whose contribution to the emission decay was negligible at lower excitation pulse intensities. In all these studies no attention was given to the tacticity and molecular weight distribution of the used PVP, although it has clearly been pointed out in the past[10] that these polymer characteristics have a marked effect on the excited-state properties of aryl vinyl polymers.

In this work we report on the excited-state properties (spectral and time dependent) of a well-characterized, high molecular weight PVP as studied by fluorimetry, single-photon-counting, and laser flash photolysis techniques. Also spectroscopic evidence is presented for the formation of vinylpyrene-like moieties in the UV-induced photochemical degradation of PVP in dilute degassed THF solution.



Experimental Section

1-Vinylpyrene and poly(1-vinylpyrene) were synthesized as described in a previous paper.[9] 1-Ethylpyrene was obtained from Molecular Probes Inc. and used without further purification. The molecular weight was determined by gel permeation chromatography (GPC) with four μStyragel columns (10^5, 10^4, 10^3 and 500 Å) calibrated with polystyrene standards and with THF as the eluant at a flow rate of 2 mL/min. The detection system was a Varian Vari-Chrom UV/VIS spectrophotometer set at 290 nm. Proton and ^{13}C NMR spectra were determined with a NIC NB-300 spectrometer in deuteriochloroform with Me_4Si as internal standard. UV spectra were determined in THF (Aldrich, spectrophotometric grade, Gold Label, inhibitor free) with a Cary Model 219 spectrophotometer. Fluorescence spectra were recorded on a SLM 8000 single-photon-counting fluorescence spectrometer, equipped with a microprocessor capable of correcting the recorded fluorescence spectra for instrumental distortions. The solutions were deaerated by thorough purging with oxygen-free argon. Optical density at the excitation wavelength was less than 0.1. Polymer films were prepared by slow evaporation of a 10 wt % THF solution of the polymer from the bottom of a beaker. Thin films formed by this method were optically clear on visual inspection.

Quantum yields were determined with quinine sulfate as a standard ($\phi_{FM} = 0.558$ at 20 °C). Singlet lifetimes were determined with a single-photon-counting fluorescence lifetime apparatus (Photochemical Research Associates Inc.) as described elsewhere.[11]

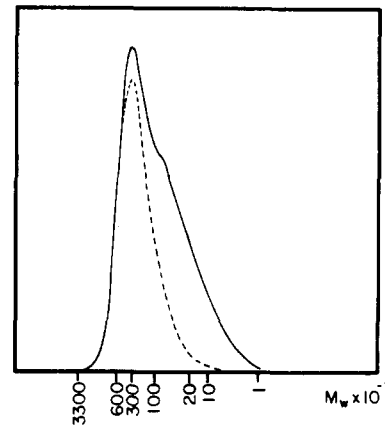


Figure 1. GPC elution profile of PVP: (—) after workup of the reaction mixture and (---) after fractionation. Molecular weights are relative to polystyrene standards.

Flash photolysis experiments were performed with a 337-nm laser pulse (2–3 mJ, pulse width 8 ns) from a Molectron UV-400 nitrogen laser system or a 355-nm laser pulse (80 mJ, pulse width 6 ns) from a Quanta-Ray Nd–YAG laser system. A typical experiment consisted of 10–20 replicate shots per sample, and the average signal was processed with a LSI-11 microprocessor interfaced with a PDP-11/55 computer. The details of the experimental procedure can be found elsewhere.[12a-c] The time-resolved emission spectrum of poly(1-vinylpyrene) was recorded with the same laser flash photolysis setup and was later corrected for photomultiplier response.

The extinction coefficient of triplet 1-pentylpyrene was determined by the sensitization technique described by Bensasson and Land.[12d] Biphenyl triplets were generated in benzene by using a pulse radiolysis technique. Deaerated solutions of benzene containing 0.05 M biphenyl were irradiated with 5-ns electron pulses from the Notre Dame 7-MeV ARCO LP-7 linear accelerator using dose rates of $\sim 2 \times 10^{16}$ eV/g per pulse.[12e] The energy transfer from the triplet biphenyl to 1-pentylpyrene was monitored by recording the time-resolved absorption spectra of the transients. The extinction coefficient of triplet 1-pentylpyrene (ϵ_a) was determined from the expression[12d]

$$\epsilon_a = \epsilon_d \frac{(\Delta OD)_a}{(\Delta OD)_d} \frac{k_2}{k_2 - k_1}$$

where ϵ_d is the extinction coefficient of triplet biphenyl, $(\Delta OD)_a$ and $(\Delta OD)_d$ are the observed absorbance maxima of triplet 1-pentylpyrene and triplet biphenyl, and k_1 and k_2 are the rate constants for the triplet biphenyl decay in the absence and in the presence of 1-pentylpyrene.

Photolysis of thoroughly deaerated THF solutions of PVP was performed in a Rayonet Photochemical reactor equipped with 16 RPR-3000 Å lamps. The quantum yield of polymer degradation was determined with a setup of a 150-W xenon lamp and a Bausch and Lomb monochromator and hexamethylenebismaleimide as actinometer.[13] The quantum yield of random scission was obtained according to a method described by Fox et al.[14] 2-Methyltetrahydrofuran was twice distilled over $LiAlH_4$ prior to use. The IR spectrum was taken on a Bomem FT-IR spectrometer.

Results and Discussion

Spectroscopic Characterization of Poly(1-vinylpyrene). Polymerization of 1-vinylpyrene with Ziegler–Natta catalyst (1:1 $AlEt_3/TiCl_4$ catalyst and 1:50 catalyst/monomer) in benzene at 80 °C for 24 h, and after workup with MeOH/HCl resulted in a white solid.[9] Purification of poly(1-vinylpyrene) by dissolution in THF, followed by reprecipitation with methanol (3 times), yielded a high molecular weight poly(1-vinylpyrene), which showed a bimodal molecular weight distribution as can be seen in Figure 1 in a typical GPC elution profile. A fraction with a $\bar{M}_w$ of 320 000 and a polydispersity of 1.15 was

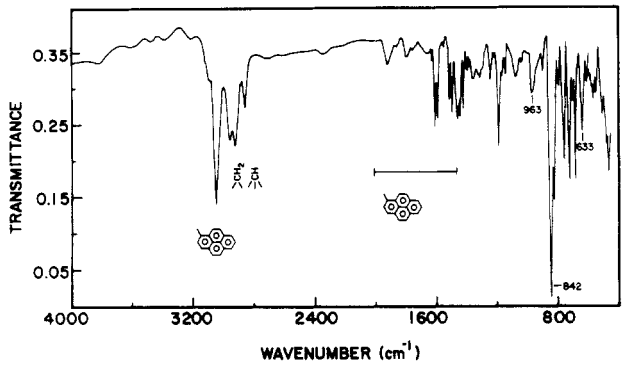


Figure 2. FTIR spectrum of PVP film.

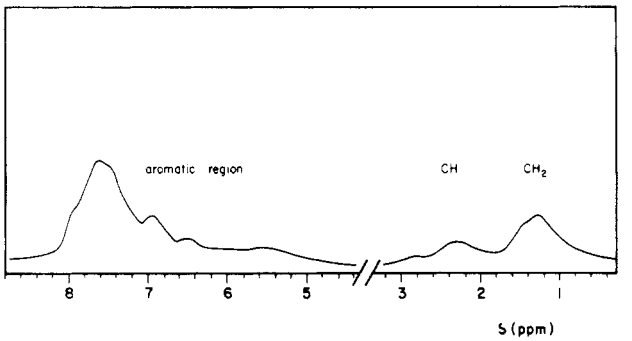


Figure 3. ^1H NMR spectrum of PVP in $CDCl_3/Me_4Si$.

obtained by adding increments of 2-propanol to a THF solution of the polymer.

PVP is soluble in THF and $CHCl_3$ and 5 wt % solutions can be prepared easily in these solvents. In the case of CH_2Cl_2, a 0.5 wt % solution was obtained as this solution indicated little turbidity; however, with benzene and toluene only very dilute solutions were possible. It has a softening temperature around 280 °C and it possesses a high degree of crystallinity as evidenced by its high birefringence when examined under a polarizing hot-stage microscope.

The FT-IR spectrum (Figure 2) clearly shows the disappearance of the absorptions of the vinyl group (910 and 990 cm^{-1}) in 1-vinylpyrene and is in accordance with the spectrum published earlier for a PVP sample prepared with radical initiators (benzoyl peroxide or di-*tert*-butyl peroxide).[15] The ^1H NMR spectrum in $CDCl_3$ at room temperature (Figure 3) exhibits poor resolution and is typical of high molecular weight vinyl polymers. On the basis of the area under the peaks the region of the spectrum downfield from δ 5.0 corresponds to the aromatic protons, while the remaining three backbone protons are upfield from this value. The magnitude of the shielding of the aromatic protons, which is much larger than that found in the ortho protons of polystyrene,[16] but comparable to that observed in poly(*N*-vinylcarbazole),[17] reflects the bulkiness of the pyrenyl groups and their mutual interaction. PVP appears therefore to represent a polymeric environment with high steric and spatial constraint in which the aromatic groups are tightly packed, resulting in large magnetic anisotropies.

Information about the tacticity of the polymer can be derived from the totally proton-decoupled ^{13}C NMR spectrum. From Figure 4a, it is clear that the resonances of all the carbon atoms are affected by the polymer stereochemistry. In contrast to the case in various polystyrenes even the signal associated with the methine carbon (C_α) is not only broadened but seems to consist of different peaks. However, the strongest effects of polymer structure are seen on the aromatic C_1 and methylene C_β resonances,

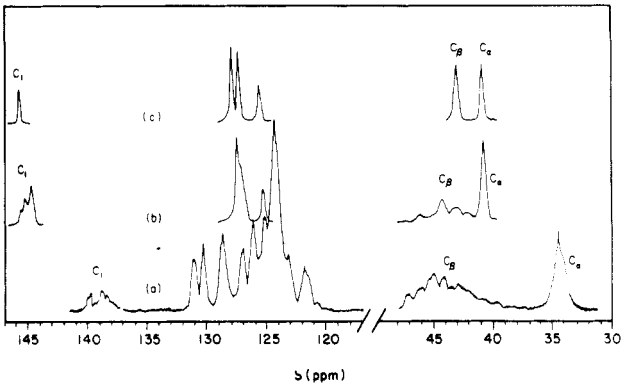


Figure 4. $^{13}C\{^1H\}$ NMR spectrum of (a) PVP, (b) atactic polystyrene,[18] and (c) isotactic polystyrene[18] in $CDCl_3$.

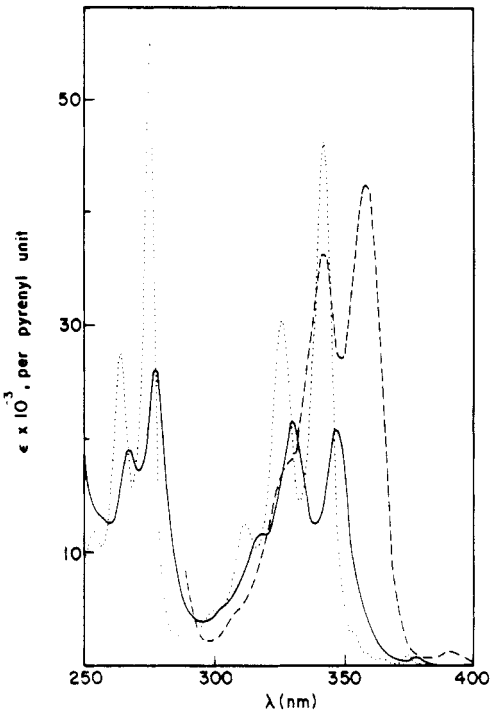


Figure 5. UV spectra of PVP (—), 1-vinylpyrene (---) and 1-pentylpyrene (···) in THF.

and from this it should in principle be possible to determine the exact microtacticity if at least one stereoregular polymer or oligomer with known structure is available.[18] Since (1) this is not the case, and (2) the whole of the above is possibly complicated by the occurrence of different rotamers due to the nonsymmetric attachment of the pyrenyl group to the polymer backbone, we will restrict ourselves to a comparison of the picture obtained for the C_1 and C_β resonances in PVP with the one obtained for the corresponding resonances in various polystyrenes (Figure 4). From this figure it is clear that we deal with a polymer that is mainly "atactic" in character, although some tetrad or pentad sequences may be preferred over others as follows from the nonequal intensity distribution of these sequences in the C_1 and C_β signals of PVP. It is interesting to note that PVP obtained with Ziegler–Natta catalyst is atactic, whereas the use of this catalyst in the polymerization of styrenes yields isotactic polymers. At this point it is worthwhile to remention the high crystallinity observed in this atactic PVP. We believe that it is caused by the side chain–side chain interactions, which seem to be the driving force in atactic polymers with bulky side groups.[19]

The absorption spectra in THF solution at room temperature for PVP and the monochromophoric 1-pentyl-

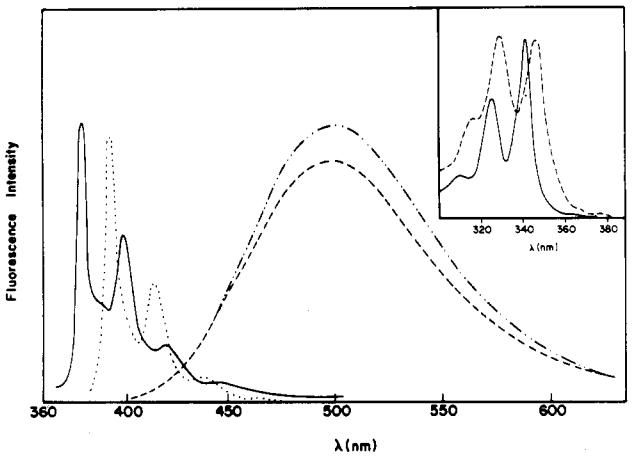


Figure 6. Fluorescence spectra of PVP film (---) and of THF solutions of PVP (-·-·-), 1PP (—), and 1-vinylpyrene (···) at room temperature (λ_{exc} = 330 nm). Inserted are the excitation spectra of 1PP (—) (analyzed at 380 nm) and PVP (---) (analyzed between 450 and 550 nm) in THF solution at room temperature.

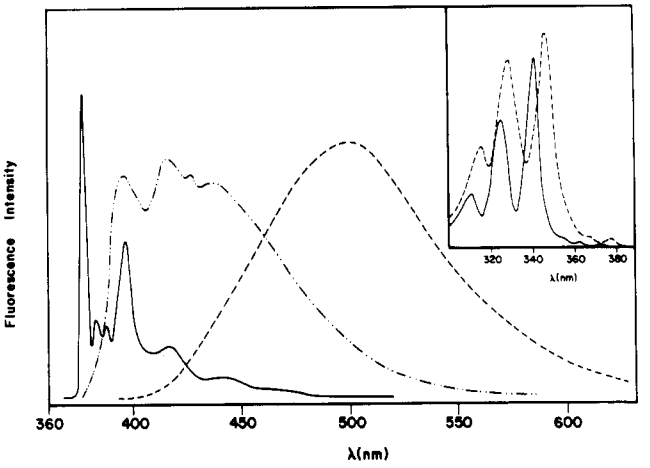


Figure 7. Fluorescence spectra of PVP film (---) and of MTHF solutions of PVP (-·-·-) and 1PP (—) at 77 K (λ_{exc} = 330 nm). Inserted are the excitation spectra of 1PP (analyzed at 380 nm) (—) and PVP (---) (analyzed at 480 nm) in MTHF solution at 77 K.

pyrene, 1PP, which is used in this study as the reference compound, are shown in Figure 5. The ^1L_b–^1A, ^1L_a–^1A and ^1B_b–^1A bands of PVP are red-shifted by about 4, 5, and 3 nm, respectively, and show a dramatic decrease in molar absorptivity when compared to those of 1PP. Until now no such large hypochromism (23, 22, and 18% for the ^1L_b–^1A, ^1L_a–^1A, and ^1B_b–^1A bands, respectively) has been reported for aromatic vinyl polymers, but it has been observed in the absorption spectra of several anthracene dimers[20] and some native polynucleotides[21,22] in which a strong interaction between the absorbing chromophores exists. Both the red-shift and the hypochroism in PVP can only adequately be explained if a considerable overlapping between pyrenyl moieties occurs; the red-shift will be a result of the change in the dispersion energy and static interaction energy between two pyrenyl groups when one is electronically excited, whereas the hypochrosim will originate either from dispersion force interactions[22] or from configuration mixing between different excited states.[20] Strictly spoken, the above explanation is only valid if an ordered array of interacting chromophores is assumed in the polymer.[21] However, at this moment it is not clear if the preferred occurrence of some pentad sequences, as follows from the ^{13}C NMR spectrum, induces enough order in the solution conformation of PVP to give rise to the observed effects. In any case, the UV spectrum of PVP, in accordance with the results obtained from the ^1H NMR spectrum, points to a polymer in which the pyrenyl groups are tightly packed and hence interact strongly.

Table I
^1H NMR Data of PVP and *meso*- and *rac*-2,4-Di(1-pyrenyl)pentane in $CDCl_3/Me_4Si$ at 25 °C

compd	aromatic	CH_3	CH_2	CH
mesoDPP[a]	7.93–8.22	1.54	2.44	3.95
racDPP[a]	7.05–8.22	1.49	2.53	3.71
PVP	5.0–8.2		0.8–1.6	1.8–3.2

[a] Reference 6.

Table II
Quantum Yields of Monomer (ϕ_{FM}) and Excimer (ϕ_{FD}) Fluorescence of PVP and 1PP

compd	solvent	temp, K	$\phi_{F,tot}$	ϕ_{FM}	ϕ_{FD}
1PP	THF	298	0.87	0.87	
PVP	THF	298	0.44		0.44
	CH_2Cl_2	298	0.44		0.44
PVP[a] (low $\bar{M}_w$)	THF	298	0.415	0.005	0.41
PVP	MTHF	77	0.89		

[a] $\bar{M}_w$ = 7100, $\bar{M}_w/\bar{M}_n > 2$; prepared by photoelectrochemical polymerization of 1-vinylpyrene on CdS in CH_3CN.[23]

Table III
Emission Maxima and FWHH of the Excimer Band of PVP as a Function of Excitation Wavelength and Temperature

λ_{exc}, nm	T, K	$\lambda_{FD,max}$, nm	FWHH, cm^{-1}
275	298	498	3730
340	298	498	3785
330	358	490	4224
330	200	500	3735

Fluorescence Properties. Fluorescence Spectra. The polymer fluorescence spectra of THF solutions (at room temperature) and MTHF glasses (at 77 K) are summarized in Figures 6 and 7. Also in these figures are shown the neat-film and 1PP spectra at room temperature and at 77 K. We note that the spectra of PVP taken at room temperature for both solution and neat film are very similar and are characterized by a broad structureless emission at 500 nm and a complete lack of monomer fluorescence. Only for a PVP sample of low $\bar{M}_w$ and high polydispersity ($\bar{M}_w$ = 7100, $\bar{M}_w/\bar{M}_n > 2$)[23] a small amount of monomer fluorescence was observed (Table II). The excitation spectra analyzed between 450 and 550 nm (insert Figure 6) matched well with the absorption spectrum as regard to the position and shape but differ slightly in the ratio of the different vibrational bands. At 77 K a different picture emerges for the MTHF solution when compared with the spectra at room temperature: a structured emission shows up between 380 and 440 nm, together with a structureless fluorescence band around 460 nm. The spectrum of the neat film at 77 K still consists of a broad emission at 500 nm. However, it extends more to the blue than the one at room temperature. The excitation spectra of the MTHF glass, analyzed between 400 and 480 nm, are again very similar to the absorption spectrum of PVP, though an increase in vibronic structure occurred, which is a common feature observed at lower temperatures.[24]

Let us consider the results obtained in fluid THF solution. The width at half-maximum of the excimer emission band was found to be excitation wavelength and temperature dependent (Table III). Furthermore the maximum of the excimer fluorescence showed a bathochromic shift with decreasing temperature. These data suggest the existence of more than one excimer. This fact is more evi-

Table IV
Variation of the Decay Parameters as a Function of the Analysis Wavelength (λ_{AN}) in the Excimer Region of PVP in THF

λ_{exc}	λ_{AN}	T	α_1	τ_1	α_2	τ_2	α_2/α_1	χ^2
330	460	298	0.020	38	0.068	126	3.40	1.10
330	500	298	0.011	42	0.049	127	4.45	1.13
330	550	298	0.002	39	0.013	123	6.50	1.04
275	500	298	0.009	40	0.027	130	3.00	0.94
330	480	200	0.013	97	0.011	184	0.85	0.99
330	530	200	0.011	99	0.005	197	0.45	1.07

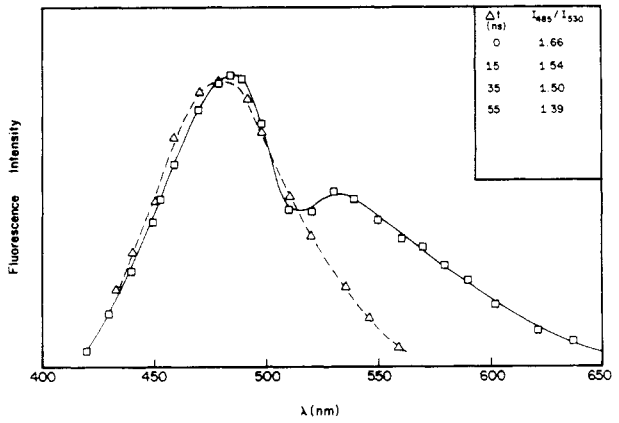


Figure 8. Time-resolved emission spectra for PVP (—) in THF (Δt = 0 ns) and for a concentrated solution of 1PP (---) in cyclohexane (Δt = 0 ns) (355-nm laser pulse excitation). Inserted are the ratios of fluorescence intensities I_{480}/I_{530} for PVP as a function of the delay time (Δt).

dent in the fluorescence decay measurements.

Lifetime Measurements. Analyzing the fluorescence decay at different wavelengths in the excimer band clearly indicated the existence of two decaying species with a different decay time and a different spectral distribution (Table IV). This indicated the presence of two excimers with a different geometry in PVP solutions. It must be noted that the fitting of the excimer decay curves to a sum of the two exponentials yielded very good reduced χ^2, and no triple-exponential functions were necessary. No rise time was observed at room temperature, which suggested that the excimer buildup in PVP is very fast and occurs in the subnanosecond time scale. This can be understood if one takes into account the results from the lifetime measurements on meso-2,4-di(1-pyrenyl)pentane[6] (mesoDPP) and compares the conformational data available for this compound with the one for PVP. In mesoDPP excimer rise times of several nanoseconds are observed, which are related to the rotations necessary to achieve an excimer conformation. This compound is known to lack interactions between pyrenyl groups in the ground state. Unlike mesoDPP, PVP shows strong interactions in the ground state as evidence by UV and ^{1}H NMR spectroscopy, which opens the possibility of either preformed excimer sites or conformations in which only minor conformational changes have to occur in order to achieve the excimer conformation(s). These are clearly processes in the picosecond time domain.

In THF at 200 K we obtain a similar picture for the fluorescence spectrum as the one obtained at room temperature, except for the presence of a very small amount of monomer. The decay curves in the excimer region can again be fitted to a sum of two exponentials, and the ratio of the preexponentials shows a dependence on the analysis wavelength (Table IV).

Time-Resolved Emission Spectra. The existence of two excimers in PVP was also demonstrated by recording time-resolved emission spectra in THF at room temperature (Figure 8). The emission profiles are consistent with

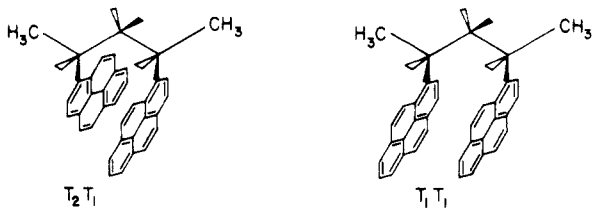


Figure 9. Possible structure for the eclipsed (T_1T_1) and staggered (T_2T_1 or T_1T_2) excimer conformation in *meso*-2,4-di(1-pyrenyl)pentane.[6]

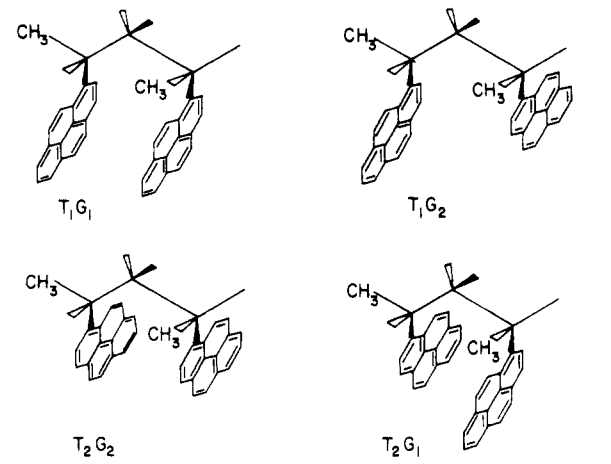


Figure 10. Possible structure for the eclipsed (T_2G_2 and T_1G_1) and staggered (T_1G_2 and T_2G_1) excimer conformations in *rac*-2,4-di(1-pyrenyl)pentane.

the presence of two spectrally distinct species with wavelength maxima at 485 and 530 nm. The decrease of the ratio of fluorescence intensities I_{485}/I_{530} with longer delay times suggested that the 485- and 530-nm species can be related to the shorter (40 ns) and longer lived (125 ns) excimer, respectively. In contrast, the excimer generated from a concentrated solution of 1PP exhibited a single emission band (λ_{max} = 480 nm) under similar conditions.

Excimer Configuration. In their study of excimer formation in mesoDPP Collart et al.[6] proposed a staggered and an eclipsed excimer conformation as depicted in Figure 9 in order to explain the dual excimer fluorescence. Atactic PVP is composed not only of isotactic but also of syndiotactic diads and for the latter ones staggered and eclipsed excimer conformations are possible too (Figure 10). However, of these four conformations, steric interaction between the methylene group and the peri-hydrogens makes the T_2G_2 conformation a highly unstable one, whereas steric interaction between the peri-hydrogen on one of the pyrenyl groups and the methyl group makes the T_2G_1 and T_1G_1 conformations less probable. Furthermore in the polymer the methyl group is replaced by the rest of the polymer chain, which induces even more steric hindrance and makes these conformations highly unstable. This means that for atactic PVP the following excimer conformations are the most probable ones: eclipsed T_1T_1 and staggered T_2T_1 or T_1T_2 in meso diads and staggered T_1G_2 in racemic diads. If we assume that the meso and

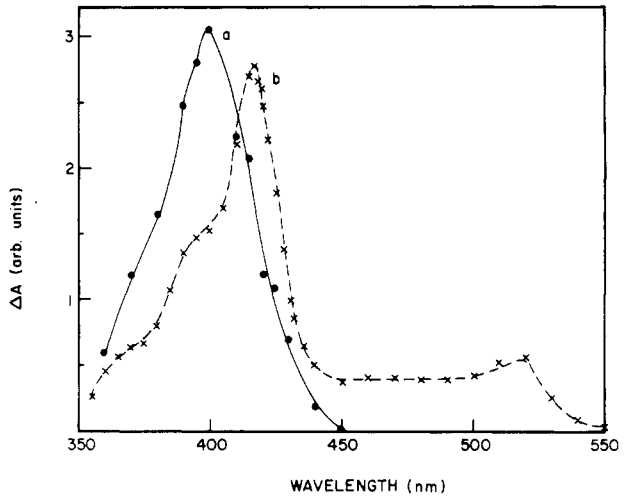


Figure 11. Triplet–triplet absorption spectra of PVP (●) and 1PP (×) in THF at room temperature.

racemic staggered excimer conformations have comparable photophysical properties as they have the same degree of overlap between the two aromatic moieties and about the same conformational stability, the dual excimer fluorescence in atactic PVP can be related to the occurrence of eclipsed and staggered excimer conformations.

Let us now consider the emission data obtained in a rigid matrix at 77 K. A structured emission shows up between 380 and 440 nm, which is broadened and red shifted by about 20 nm when compared to that of the model compound 1PP. Similar effects have been observed for P2VN in cyclohexane matrix[1f] and for samples of poly(9-anthrylmethyl ethenyl ether)[25] and can be ascribed to fluorescence from excited ground-state dimers.

In order to explain the structureless fluorescence emission around 480 nm the following facts must be considered:

1. The emission in the region of 480 nm coincides with the one attributed to the staggered excimer in fluid solution.

2. Its decay curve, analyzed at 480 nm in a MTHF matrix, can be fitted to a difference of two exponentials, yielding a rise time of 7.3 ns and a decay time of 99 ns.

3. The formation of a staggered excimer conformation from either T_2G_1 or T_2T_1 conformations in meso and racDPP,[6] respectively, requires rotations of less than 120° as only a partial overlap of the two pyrenyl groups is necessary. In the PVP polymer even smaller rotations are required, as we know from ^1H NMR and UV spectra that strong interactions already exist in the ground state.

From these observations it can be concluded that the longer wavelength band at 77 K most probably originates from a staggered excimer. Though ground-state dimer formation occurs at 77 K, the fact that at 77 K a rise time is observed for the high-energy excimer and that the low-energy excimer is absent rules out the occurrence of "preformed excimer sites" in PVP. With regard to the film spectra at room temperature and at 77 K, it is sufficient to note that they are very similar to that of a THF solution at room temperature and that the decay curve analyzed at 500 nm as a sum of two exponentials gave decay times of 23 and 80 ns, respectively, thereby suggesting the presence of two types of excimers too. These shorter lifetimes, when compared to those in THF solution, are probably caused by oxygen quenching as the experiment was performed in air.

In closing this section one comment concerning the fluorescence decay curves collected at wavelengths lower than 460 nm in fluid solution is in order. Analysis to a sum of two exponentials is not adequate anymore and the presence of a third decay component becomes evident, particularly at lower temperatures. Whether this is due to the emission from an excited ground-state dimer or from a monomer is not clear yet.

Table V
Transient Absorption Characteristics of 1PP and PVP in THF at Room Temperature

compd	λ_{max}, nm	lifetime, μs	$\epsilon_{\lambda_{max}}$	ϕ_T
1PP	416	155[a]	37 000[a]	0.15
PVP	400			$\leq 10^{-3}$

[a] Benzene solution.

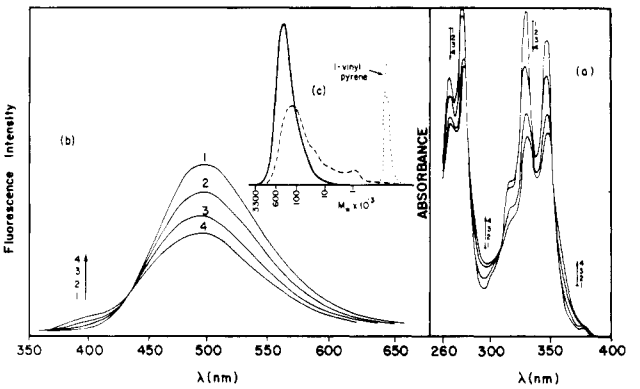


Figure 12. UV spectra (a) and emission spectra (b) of PVP as a function of irradiation time at 280 nm in deaerated THF: (1) 0 min, (2) 52 min, (3) 197 min, (4) 307 min. GPC elution profile of PVP before (—) and after irradiation (---) at 300 nm in deaerated THF.

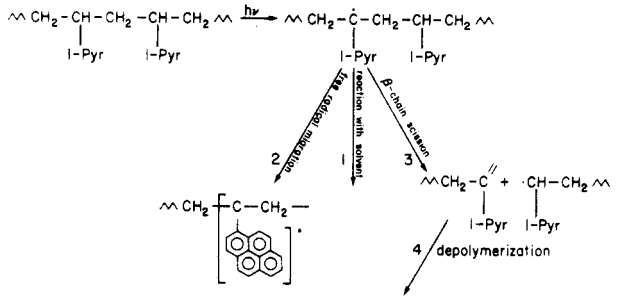
Triplet Characteristics. The triplet absorption spectrum of poly(1-vinylpyrene) obtained with direct excitation of a 337-nm laser pulse is shown in Figure 11. Quenchers such as O_2 were found to quench the transient absorption. The observed absorption maximum ~400 nm is very similar to the triplet absorption maximum reported for other pyrene compounds.[26,27] For comparison, the triplet absorption spectrum of 1PP (λ_{max} = 416 nm) is also shown in Figure 11. Repeated pulsing of the same solution resulted in the photoscission of the polymer (see next section) and as observed earlier[28] the vinyl conjugated pyrene moieties exhibited transient absorption in the region of 380–550 nm which interfered with the triplet absorption measurements. Hence care was taken to employ a flow cell to flow in fresh sample before excitation with the laser pulse.

The triplet quantum yield was measured from the flash photolysis experiment with a 337-nm laser pulse as the excitation source and anthracene triplet as reference (ϕ_T = 0.7, ϵ_{422} = 64 700 M^{-1} cm^{-1}).[29] While the triplet yield of 1PP was comparable to that of other pyrene compounds,[26,27] PVP exhibited a relatively very low triplet quantum yield ($\leq 10^{-3}$, Table V). Highly efficient excimer formation competed with the deactivation of the excited singlet by intersystem crossing.

Photostability. PVP, like polystyrene,[30,31] is found to be photoactive. In deaerated THF solution, irradiation of the polymer at wavelengths of 350 nm or less leads to photodegradation as shown by a decrease of the molecular weight as determined by GPC (Figure 12). When a scheme for the photolysis of PVP in solution, is put forward, the following facts have to be considered:

1. In the absorption spectrum an increase in the absorbance occurs in the wavelength region 352–390 nm, where vinyl conjugated pyrene has a strong absorption

Scheme I



band. This is furthermore accompanied by a decrease in the normal PVP absorption (310–350-nm region) (Figure 12).

2. The fluorescence spectrum shows besides the excimer band a new emission between 380 and 430 nm, which is characteristic of vinyl conjugated pyrene. The excitation spectrum taken at 400 nm is very similar to the absorption spectrum of 1-vinylpyrene.

3. Thin-layer chromatography (SiO_2/toluene) of a photolyzed solution does not reveal any presence of pyrene, ethylpyrene, or 1-vinylpyrene.

4. The GPC chromatogram is indicative of the fact that formation of monomers is negligible but that chain scission occurs.

5. The quantum yields for the disappearance of normal PVP absorption, ϕ_d, for the formation of vinyl conjugated pyrene moieties, ϕ_f, and for the random scission, ϕ_s, are 8.0×10^{-5}, 1.5×10^{-5}, and 1.1×10^{-5}, respectively.

This leads to a tentative scheme (Scheme I)[32] in which the predominant primary process is a tertiary carbon–hydrogen bond fission, in accordance with the results obtained for polystyrene.[30,31]

Secondary processes can be described as (1) reaction of the resulting macroradical with the solvent, (2) free radical migration from the main chain to the pyrenyl side group, followed by reaction with the solvent, which results in a destruction of the aromatic pyrenyl system, and (3) main-chain scission, which gives rise to the formation of unsaturated chain ends. This latter reaction also leads to an end-chain radical, which in principle is capable of depolymerizing.[31] The fact that no or only traces of monomer were detected suggests that the most probable reaction pathways of this radical are (1) and (2).

Conclusion

Though studies[6] on bichromophoric model compounds suggest a complex behavior for intramolecular excimer formation in atactic PVP in fluid solution, a rather simple picture emerges: two excimers are formed, with a different lifetime and a different spectral distribution as evidenced by both lifetime measurements and time-resolved emission spectra. We attribute the high- and low-energy excimers to staggered and an eclipsed conformations, respectively. The quantum yield for the triplet formation is very low ($\phi_T \leq 10^{-3}$), and no triplet excimers could be detected from the transient absorption spectra. Finally, photolysis experiments are indicative of the fact that PVP is relatively a stable polymer ($\phi_{scission} \approx 10^{-5}$) in which the pyrenyl groups act as an "energy sink", through which the energy of radiation can be dissipated mainly through excimer fluorescence and internal conversion to the ground state.

Acknowledgment. We thank Prof. F. C. DeSchryver for helpful discussions, Dr. R. Kessler for recording FT-IR spectra, and Mr. D. Schifferl for recording NMR spectra. The research described herein was supported by the Office of Basic Energy Sciences, Department of Energy. This is Document No. NDRL-2792 from the Notre Dame Radiation Laboratory.

Registry No. PVP, 25120-43-8; 1PP, 80655-41-0.

References and Notes

(1) (a) Ghiggino, K. P.; Wright, R. D.; Phillips, D. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1499. (b) Phillips, D.; Roberts, A. J.; Rumbles, G.; Soutar, I. *Macromolecules* **1983**, *16*, 1198. (c) Phillips, D.; Roberts, A. J.; Soutar, I. *Polymer* **1981**, *22*, 427. (d) Gupta, A.; Liang, R.; Mocanin, J.; Kliger, D.; Goldenbeck, R.; Horwitz, J.; Miskowski, V. M. *Eur. Polym. J.* **1981**, *17*, 485. (e) Demeyer, K.; Van der Auweraer, M.; Aerts, L.; De Schryver, F. C. *J. Chim. Phys.* **1980**, *77*, 493. (f) De Schryver, F. C.; Demeyer, K.; Van der Auweraer, M.; Quanten, E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 93. (g) Ng, D.; Guillet, J. E. *Macromolecules* **1981**, *14*, 405. (h) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697. (i) Hoyle, C. E.; Nemzek, T. L.; Mar, A.; Guillet, J. E. *Macromolecules* **1978**, *11*, 429. (j) Ghiggino, K. P.; Archibald, D. A.; Thistlethwaite, P. J.; *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 673. (k) Kauffman, H. F.; Weixelbaumer, W.-D.; Buerbaumer, J.; Schmoltner, A.-M.; Olaj, O. F. *Macromolecules* **1985**, *18*, 104. (l) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 31. (m) Alexandru, L.; Somersall, A. C. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2013. (n) Morawetz, H. *Science (Washington, D.C)* **1979**, *203*, 405. (o) Nishijima, Y. *J. Macromol. Sci., Phys.* **1973**, *B8*, 389. (p) Beavan, S. W.; Hargreaves, J. S.; Phillips, D. *Adv. Photochem.* **1979**, *11*, 207. (q) Somersall, A. C.; Guillet, J. E. *J. Macromol. Sci., Rev. Makromol. Chem.* **1975**, *C13*, 135. (r) Nishijima, Y. *Prog. Polym. Sci. Jpn.* **1973**, *6*, 199. (s) Ghiggino, K. P.; Roberts, A. J.; Phillips, D. *Adv. Polym. Sci.* **1981**, *40*, 106.

(2) (a) De Schryver, F. C.; Moens, L.; Van der Auweraer, M.; Boens, N.; Monnerie, L.; Bokobza, L. *Macromolecules* **1982**, *15*, 64. (b) Itagaki, H.; Horie, K.; Mita, I.; Washio, M.; Tagawa, S.; Tabata, Y.; Sato, H.; Tanaka, Y. *Chem. Phys. Lett.* **1985**, *120*, 547.

(3) De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406.

(4) De Schryver, F. C.; Demeyer, K.; Toppet, S. *Macromolecules*, **1983**, *16*, 89.

(5) Collart, P.; Demeyer, K.; Toppet, S.; De Schryver, F. C. *Macromolecules* **1983**, *16*, 1390.

(6) Collart, P.; Toppet, S.; Zhou, Q. F.; Boens, N.; De Schryver, F. C. *Macromolecules* **1985**, *18*, 1026.

(7) McDonald, J. R.; Echols, W. E.; Price, T. R.; Fox, R. B. *J. Chem. Phys.* **1972**, *57*, 1746.

(8) Yokoyama, M.; Tamamura, T.; Nakano, T.; Mikawa, H. *Chem. Lett.* **1972**, 499.

(9) Kamat, P. V.; Basheer, R.; Fox, M. A. *Macromolecules* **1985**, *18*, 1366.

(10) (a) Fitzgibbon, P. D.; Frank, C. W. *Macromolecules* **1982**, *15*, 733. (b) Ito, S.; Yamamoto, M.; Nishijima, Y. *Rep. Prog. Polym. Phys. Jpn.* **1976**, *19*, 421. (c) Nichijima, Y.; Mitani, K.; Katayama, S.; Yamamoto, M. *Rep. Prog. Polym. Phys. Jpn.* **1970**, *13*, 421. (d) Ishii, T.; Handa, T.; Matsunaga, S. *Macromolecules* **1978**, *11*, 40. (e) Torkelson, J.; Lipsky, S.; Tirrell, M. *Macromolecules* **1981**, *14*, 1603. (f) David, C.; Putman de Lavareille, N.; Geuskens, G. *Eur. Polym. J.* **1974**, *10*, 617. (g) David, C.; Lempereur, L.; Geuskens, G. *Eur. Polym. J.* **1974**, *10*, 1181. (h) Ishii, T.; Handa, T.; Matsunaga, S. *Makromol. Chem.* **1977**, *178*, 2351.

(11) Brett, B. R. M.; Kilp, T. *Polymer* **1984**, *25*, 989.

(12) (a) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965. (b) Das, P. K.; Bobrowski, K. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1009. (c) Chattopadhyay, S. K.; Das, P. K.; Hug, G. *J. Am. Chem. Soc.* **1982**, *104*, 4507. (d) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904. (e) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129.

(13) Put, J.; De Schryver, F. C. *J. Am. Chem. Soc.* **1973**, *95*, 137.

(14) Fox, R. B.; Price, T. R. *J. Polym. Sci., Part A* **1965**, *3*, 2303.

(15) Tanikawa, K.; Ishizuka, T.; Suzuki, K.; Kusabayashi, S.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2719.

(16) Bovey, F. A.; Hood, F. P., III; Anderson, E. W.; Snyder, L. C. *J. Chem. Phys.* **1965**, *42*, 3900.

(17) (a) Williams, D. J. *Macromulecules* **1970**, *3*, 602. (b) Limburg, W. W.; Williams, D. J. *Ibid.* **1973**, *6*, 787.

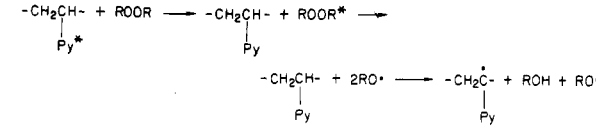
(18) Inoue, Y.; Nishioka, A.; Chûjô, R. *Makromol. Chem.* **1972**, *156*, 207.

(19) Standt, U. D. *J. Macromul. Sci., Rev. Macromol. Chem. Phys.* **1983**, *C23*, 317.

(20) Ferguson, J.; Mau, A. W.-H.; Morris, J. M. *Aust. J. Chem.* **1973**, *26*, 91.

(21) Tinoco, I. *J. Am. Chem. Soc.* **1960**, *82*, 4785.

(22) Rhodes, W. *J. Am. Chem. Soc.* **1961**, *83*, 3609.
(23) Kamat, P. V.; Todesco, R. V. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(24) Todesco, R.; Gelan, J.; Martens, H.; Put, J.; De Schryver, F. C. *J. Am. Chem. Soc.* **1981**, *103*, 7304.
(25) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1984**, *17*, 235.
(26) Slifkin, M. A.; Walmsley, R. H. *Photochem. Photobiol.* **1971**, *13*, 57.
(27) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *Photochem. Photobiol.* **1983**, *38*, 141.
(28) Kumar, C. V.; Basheer, R. A., unpublished results.
(29) Amand, B.; Bensasson, R. *Chem. Phys. Lett.* **1975**, *34*, 44.
(30) Rånby, B.; Rabek, J. F. *Photodegradation Photo-oxidaton and Photostabilization of Polymers*; Wiley: New York, 1975; p 165.
(31) Grassie, N.; Scott, G. *Polymer Degradation and Stabilization*, Cambridge University Press: Cambridge, 1985; p 78.
(32) As suggested by one of the referees, an alternate possibility for the formation of the macroradical would involve H-atom abstraction by free radicals generated in the solution as given in the following scheme:



Investigation of Purity and Fluorescence of Poly[N^6-(9*H*-carbazol-9-ylcarbonyl)-L-lysine] Preparations

Kim Clausen* and Kay Brunfeldt

Instituttet for Kemiindustri, The Technical University of Denmark, DK-2800 Lyngby, Denmark. *Received March 17, 1986*

ABSTRACT: It is demonstrated that a polymer previously published as a homopolymer of N^6-(9*H*-carbazol-9-ylcarbonyl)-L-lysine is in fact a terpolymer of N^6-(9*H*-carbazol-9-ylcarbonyl)-L-lysine with N^6-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine and N^6-(2-methyl-9*H*-carbazol-9-ylcarbonyl)-L-lysine (ratio ca. 200:1:1). Spectroscopy and HPLC and GC/MS analysis on acid hydrolysates were applied for elucidation. The N^6-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine is shown to be the cause of the low-energy emission band observed in the fluorescence spectrum of the polymer. Previously published interpretations of fluorescence measurements are thus to be revised. 5*H*-Benzo[*b*]carbazole was synthesized as a reference compound. Commercially available carbazole preparations were found to be markedly heterogeneous.

Introduction

In recent years carbazole-based polymer systems have been the focus of considerable research due to their unusual electrical and photoelectric properties.[1-3] Several types of carbazole polymers have been synthesized and studied with a view to elucidating the photophysics of excimer formation. By far the most work has been done on poly(*N*-vinyl-9*H*-carbazole) (PVCz), which has well-documented photoelectric and excimer-forming properties.[4-6]

In order to investigate the effect of order on the photoconductive and photovoltaic behavior, Halstrøm and coworkers[7,8] prepared poly[N^6-(9*H*-carbazol-9-ylcarbonyl)-L-lysine] (PKL), which was found to have the α-helical conformation and to form a lyotropic cholesteric liquid crystal in concentrated solution. Chapoy and coworkers[9-16] used this sample in a recent series of fluorescence and photoconductivity investigations. In the following this material will be referred to as polymer I. The steady-state emission spectrum of I was reported to consist of two well-resolved emission bands at 342 and 390 nm.[9,10,12-16] Time-resolved fluorescence spectra of I were reported to reveal the presence of four emitting species, of which the two low-energy species (emitting at 386 and 408 nm) were believed to be excimers, formed from species emitting in the high-energy band.[11-13,16]

However, subsequently prepared batches of PKL turned out to differ from the first sample with respect to the low-energy emission band positioned at 390 nm. The steady-state fluorescence spectra of all new batches of PKL did only show but one unresolved emission band at 342 nm, except for highly concentrated solutions and solid films, where a shoulder corresponding to the 390-nm emission appeared. One representative of these new batches of PKL will be referred to as polymer II in the following.

This paper will report on the detection and identification of two covalently bound impurities in polymer I, viz., 5*H*-benzo[*b*]carbazole and 2-methyl-9*H*-carbazole. It will be shown that the N^6-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine moiety, although it amounts to only 0.5%, is the cause of the low-energy emission band observed in the fluorescence spectra of polymer I.

Since this paper describes the detection of trace impurities in a specific carbazole-containing polymer, the present findings and methodologies are expected to be of special interest to researchers involved with studies of carbazole-based polymer systems. However, this paper should also be of interest to researchers in the field of polymer luminescence, because in all studies on luminescence and energy transfer in polymers the purity of the samples is an outstanding problem.

Experimental Section

Apparatus. ^{1}H NMR spectra were recorded at 500 MHz on a Bruker AM 500 spectrometer. $SiMe_4$ was used as internal standard. ^{13}C NMR spectra were recorded at 22.63 and 125.7 MHz on Bruker WH-90 and AM 500 spectrometers, respectively. $CDCl_3$ and $(CD_3)_2SO$ were used as solvents. IR spectra were recorded on a Perkin-Elmer 157 G spectrophotometer using KBr disks. UV spectra were recorded on a Perkin-Elmer 320 spectrophotometer with THF, MeOH, and CH_3CN as solvents. Fluorescence spectra were recorded on a Perkin-Elmer MPF-2A spectrophotometer with dioxane and MeOH as solvents. Mass spectra were recorded on a VG 7070 F instrument operating at 70 eV using a direct inlet. Elemental analyses were carried out by Novo Microanalytic Laboratory. X-ray fluorescence analysis was carried out with a Philips TW 1410/10 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Amino acid analyses were performed on a Kontron Liquimat III amino acid

0024-9297/86/2219-2397$01.50/0