2. These results indicate that the terminal free amino groups which are inaccessible even for the Boc-Ala-OH are present in resin **3**.

Conclusion

In the competitive reactions of Boc-$(Leu_3Pro_2Gly)_n$-OH (n = 1, 2, and 4) and Boc-Ala-OH with the soluble polymer (**1**), very little decrease in the relative coupling efficiencies of the Boc-oligopeptides with increasing peptide chain length is observed as shown in Figure 1. In contrast with these observations, in the competitive reactions with cross-linked resins **2** and **3**, their relative coupling efficiencies decreased remarkably with increasing peptide chain length. These results indicate that peptide syntheses by fragment condensation on soluble polymer supports are performed with little influence of the peptide chain length of the Boc-oligopeptides consisting of up to 24 amino acid residues on the yields of coupling reactions, as long as both the carboxyl-component peptides and polymer-bound amino-component peptides have a randomly coiled structure. The "peptide segment separation" concept is demonstrated to be very useful for keeping peptides as randomly coiled structures and to be applicable for any peptide having arbitrary amino acid sequences by the insertion of temporary protecting groups into X–Y peptide bonds.[7-10] Thus, the combination of both peptide syntheses by fragment condensation on soluble polymer supports and the "peptide segment separation" concept has promising versatility for syntheses of pure large peptides and proteins, giving high coupling yields and easy processing procedures.

Registry No. Boc-(Leu_3Pro_5Gly)-OH, 91649-94-4; Boc-$(Leu_3Pro_2Gly)_2$-OH, 91649-95-5; Boc-$(Leu_3Pro_2Gly)_4$-OH, 91649-96-6; Boc-Ala-OH, 15761-38-3.

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Polymer-Modified Electrodes. Electrochemical and Photoelectrochemical Polymerization of 1-Vinylpyrene

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ABSTRACT: Polymerization of 1-vinylpyrene in acetonitrile was achieved electrochemically at a conducting SnO_2 electrode by application of anodic potentials and photoelectrochemically at a n-GaAs semiconductor electrode under visible light irradiation. Both polymers exhibited characteristic excimer emission ($\lambda_{max} \sim$ 480 nm) in both films and THF solutions similar to poly(vinylpyrene) synthesized by using Ziegler–Natta catalyst. The lifetime of the excimer emission was ~110 ns. The mechanism of photodegradation of poly(vinylpyrene) was elucidated by using ESR techniques.

Introduction

Polymer-modified electrodes have gained wider attention in recent years because of their importance in electroanalytical and photoelectrochemical applications.[1-5] Electroactive or photoactive groups can either be held electrostatically to polar groups pendent from the nonelectroactive polymer matrix or be attached directly to the backbone of the polymer. In the former type, we have recently reported some interesting features of the electrodes modified by the adsorption of poly(4-vinylpyridine) films containing some anionic dyes.[3-5] Though there have been reports of direct electropolymerization with electroactive groups directly attached to the polymer backbone (e.g. poly(vinylferrocene)[6]), little effort has been directed toward employing photoactive groups in similar polymers. The study of such polymers could reveal significant details

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regarding the photophysics of the chromophore molecules covalently attached to a long C–C chain at regular intervals. Because of the high effective concentration of the chromophore, one would expect an enhanced intermolecular interaction within the polymer coil.

Recently Bard et al.[7] and Funt et al.[8] have carried out photoelectrochemical polymerization by heterogeneous catalysis at a TiO_2 semiconductor under UV irradiation. Such a photocatalyst may not be useful for the synthesis of polymers which undergo photodegradation under UV irradiation. Narrow band gap semiconductors (perhaps n-GaAs) would be a practical choice for carrying out a visible-light-induced photoelectrochemical polymerization.

In an effort to investigate the properties of polymers with pendent photoactive aromatic functional groups we have synthesized poly(vinylpyrene) by various methods. As shown earlier, pyrene could be a useful fluorescent probe in the studies related to the macromolecular dynamics.[9,10] In this paper we present our preliminary results of electrochemical and photoelectrochemical polymerization of 1-vinylpyrene and their photophysical properties in comparison with the polymer synthesized by Ziegler–Natta catalyst. These experiments represent the first visible-light-induced photoelectrochemical synthesis of an aryl vinyl polymer at a n-GaAs semiconductor electrode.

Experimental Section

Synthesis of Materials. 1-Vinylpyrene. Pyrene-1-carboxaldehyde, obtained from Aldrich, was purified by repeated crystallization from ethanol solution. 1-Vinylpyrene monomer was synthesized from pyrene-1-carboxaldehyde by a Wittig condensation.[11] 1-Vinylpyrene was purified by column chromatography (Alumina-Basic) using 5:95 methyl *tert*-butyl ether/petroleum ether mixture under a nitrogen atmosphere in the absence of light. The monomer was then recrystallized from 5% aqueous ethanol, dried, and stored under vacuum in the absence of light (mp = 89 °C).[11]

Poly(1-vinylpyrene). 1-Vinylpyrene was polymerized by using Ziegler–Natta catalyst (1:1 $AlEt_3/TiCl_4$ catalyst and 1:50 catalyst/monomer).[11] The polymerization was carried out in Pyrex tubes connected to a high-vacuum system (10^{-6} torr). The monomer (in dry benzene) and the catalysts were introduced into the Pyrex tubes under a dry nitrogen atmosphere. Following several freeze–pump–thaw cycles, the tubes were sealed off under vacuum. The tubes were then placed in a wrist-shaker thermostat at 80 °C for 24 h. Poly(vinylpyrene) (PVP-1) was separated by precipitation with methanol and was purified several times by dissolution in THF and reprecipitation with methanol. The weight-average molecular weight of PVP-1 as determined by gel permeation chromatography was 340 000.

Other Materials. Tetrabutylammonium perchlorate (TBAP) was twice recrystallized from ethyl acetate–hexane. UV-grade tetrahydrofuran (THF) and acetonitrile from Burdick and Jackson were used as supplied.

Determination of Molecular Weight. The average molecular weight was determined by gel permeation chromatography (GPC) with four μ styragel columns (10^6, 10^5, 10^4, and 10^3 Å) and a Varian VARI-CHROM UV detector set at 260 nm with THF as the eluant. The elution curves were compared to those of monodisperse polystyrene standards.

Optical Measurements. Absorption spectra were recorded with a Cary 219 spectrophotometer. Emission spectra were recorded at room temperature with a SLM single photon counting fluorescence spectrometer. All solutions had an absorbance ≤ 0.1 at the excitation wavelength (340 nm). Emission and excitation spectra of the films coated on electrodes were measured at front face. A Teflon block was machined to accommodate a SnO_2 or n-GaAs electrode and the whole assembly could be inserted into the sample chamber of the fluorimeter.

Lifetime measurements were carried out with a flash photolysis setup using a 337-nm laser pulse (2 mJ, pulse width 8 ns) from a Molectron UV-400 nitrogen laser system as the excitation source. A typical experiment consisted of 5–10 replicate shots per sample and the average signal was processed with a LSI-11 microprocessor interfaced with a PDP-11/55 computer.

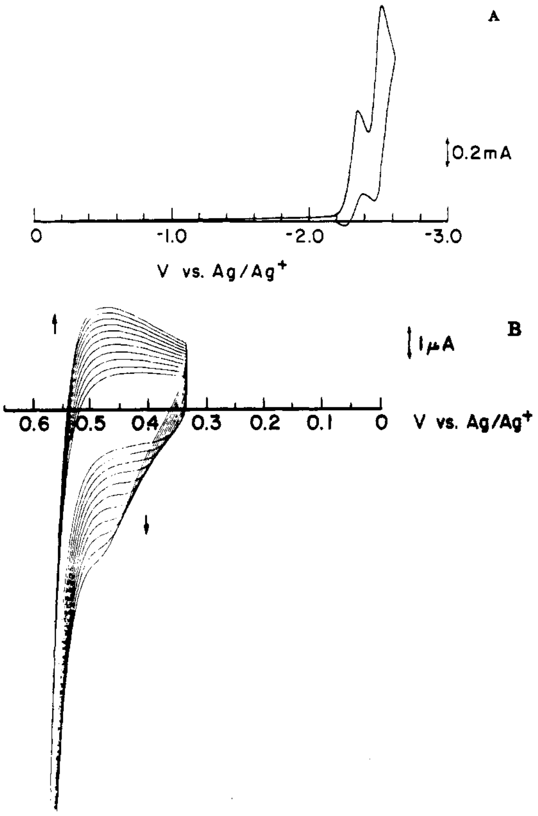


Figure 1. Cyclic voltammograms of 1-vinylpyrene in acetonitrile (0.1 M TBAP) with SnO_2 working electrode (A) during cathodic scans and (B) during anodic scans (arrows indicate increase in peak currents during successive scans). (Scan rate 20 mV/s.)

UV Photolysis. Poly(vinylpyrene) was introduced into a Spectrosil quartz tube (o.d. 5 mm) which was sealed after degassing under vacuum ($\sim 10^{-4}$ torr). The sealed tube was placed inside a liquid-N_2 Dewar flask with quartz windows and was irradiated with a light beam from a 1000-W Xe lamp passed through a heat filter. The irradiation was carried out for ca. 24 h. Trapped electrons in the quartz tube were removed by flame heating while the end of the quartz tube which contained the sample was kept at 77 K. After the tube was cooled to 77 K, the sample was allowed to slide back to the annealed end for ESR measurements.

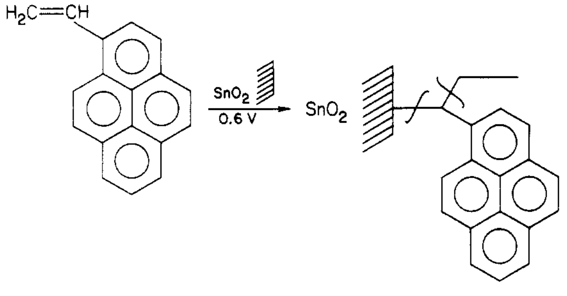
ESR Measurements. Ethe first-derivative ESR spectra were recorded with a Varian V-4500 ESR spectrometer with a dual rectangular cavity, a circulator, a bias arm, and a GaAs FET microwave amplifier. Microwave power was measured with a HP 431B power meter.

Electrochemical and Photoelectrochemical Measurements. Electrochemical and photoelectrochemical measurements were done with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 175 Universal programmer, and a Kipp and Zonen X–Y recorder. Experiments were performed in a standard three-compartment cell equipped with a Pt wire as a counter electrode and Ag/Ag^+ as a reference. For electrochemical experiments a highly conducting SnO_2 electrode, cut from transparent NESA glass (PPG industries), cleaned and dried,[4] was used as a working electrode. n-GaAs single crystal (1 mm thick, orientation: 100, $N_D \sim 10^{18}/cm^3$) employed in the photoelectrochemical experiments was a gift from M/A-COM Laser Diode Inc. Electrical contact was made by rubbing the backside of the crystal with an In/Ga alloy and connecting the shielded wire with Ag paint. The crystal was mounted onto a glass tubing support with epoxy, exposing only the flat crystal surface. The exposed area (1 cm^2) of n-GaAs crystal was etched prior to each use for 6 s in 3:1:1 concentrated H_2SO_4/30% H_2O_2/H_2O followed by a 25-s etch in 6 M HCl. The electrode was then washed with water, ethanol, and acetonitrile. The collimated light beam from a 150-W GE tungsten lamp filtered through a 460-nm cutoff filter was used for the irradiation of n-GaAs. All solutions were purged with nitrogen, and an atmosphere of nitrogen was maintained during the experiment.

Results and Discussion

Electropolymerization of 1-Vinylpyrene. Cyclic voltammograms observed under anodic and cathodic scans are shown in Figure 1. A reversible reduction peak of pyrene was observed at −2.5 V vs. Ag/Ag^+ (Figure 1A). Repetitive cathodic scans did not give any detectable evidence of electrode coating. Though the reduction of vinyl groups is feasible at potentials less than −2.5 V, such a reduction did not induce any electropolymerization. A similar failure was also observed in the electropolymerization of an anthracene derivative of methacryloyl chloride under cathodic potentials.[12]

However, when SnO_2 electrode was subjected to anodic scans (+0.3 to +0.7 V vs. Ag/Ag^+), deposition of the polymer film was seen. The oxidized form of 1-vinylpyrene as observed from the quasi-reversible peak around +0.45 V was responsible for inducing the polymerization at the SnO_2 electrode surface (reaction 1). Repetitive anodic scans led to the increase in this quasi-reversible anodic current peak (Figure 1B). It is not clear at this stage whether the propagation of the chain occurs via a cationic or a free-radical reaction. Application of higher anodic (>0.7 V) or cathodic (>−2.0 V) potentials led to the destruction of the polymer. Electrochemically deposited poly(1-vinylpyrene) (PVP-2) was insoluble in CH_3CN but was soluble in CH_2Cl_2 and THF. The polymer deposit was thoroughly washed in acetonitrile to remove any adsorbed monomer and then dissolved in THF for the optical measurements of PVP-2 in solution. The weight-average molecular weight of PVP-2 was 13 000.



(1)

(PVP-2)

Electrical efficiency of the polymerization process was determined by comparing the quantity of the polymer deposited on the electrode with the coulombs of charge utilized during the process of electropolymerization. With the passage of 1.6 mC, 6.5×10^{-8} mol of monomer units was found to polymerize on the electrode surface. This indicated that an average of four monomer units were involved in a chain reaction for every electron transferred.

Photoelectrochemical Polymerization of 1-Vinylpyrene at n-GaAs Electrode. The possibility of employing semiconductor slurries for the polymerization of methyl methacrylate was first suggested by Bard and his co-workers.[7] Funt and Tan[8] carried out polymerization of styrene at a TiO_2 single-crystal electrode. In both of these cases, it was necessary to employ UV wavelengths as the band edge of TiO_2 ($E_g \sim 3.2$ eV) lies at ~380 nm. The use of a similar large band gap semiconductor is not useful in the present experiments, since poly(vinylpyrene) photodegrades under UV irradiation. Obviously, a short band gap semiconductor such as n-GaAs ($E_g \sim 1.4$ eV) would be a better choice for the photoelectrochemical polymerization of 1-vinylpyrene as the narrower band gap of the semiconductor catalyst allows its selective excitation.

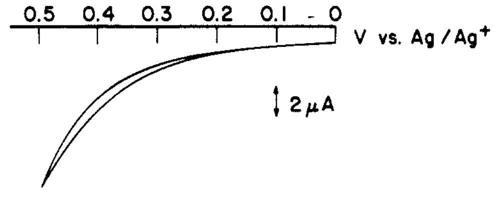


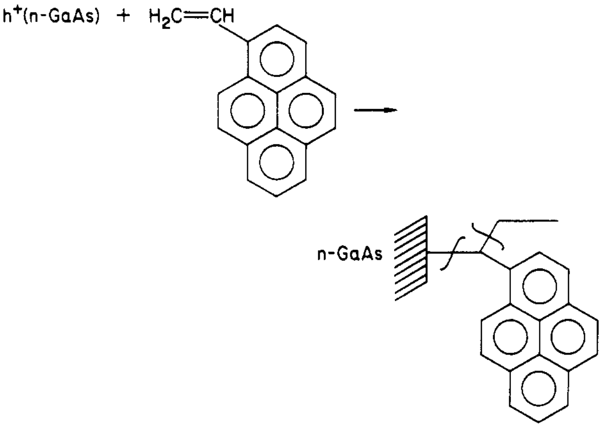
Figure 2. Cyclic voltammogram of 1-vinylpyrene in CH_3CN (0.1 M TBAP) at n-GaAs in dark (scan rate 20 mV/s).

The experimental setup for the photoelectrochemical polymerization was similar to the one employed for the electrochemical experiments. The photoanode made from a n-GaAs single crystal was dipped into a solution of 0.01 M 1-vinylpyrene in acetonitrile. As can be seen from Figure 2, no electrochemistry of 1-vinylpyrene could be seen at a dark n-GaAs electrode. Repeated anodic scans in the dark did not change the CV characteristics. However, when the electrode was exposed to light (λ > 460 nm) while held at 0 V vs. Ag/Ag^+, a large anodic current flowed through the circuit which produced a film on the electrode surface. The photocurrent then decreased slowly until a constant current of ~25 μA flowed through the circuit. After the passage of ~0.01 C, the electrode was taken out and washed carefully with acetonitrile. The polymer-modified electrode was then studied.

As established in other photoelectrochemical synthetic work, the band gap excitation of n-GaAs would result in the charge (h^+–e^-) separation within the space charge layer of the semiconductor (reaction 2). The holes migrating

$$\text{n-GaAs} \xrightarrow{h\nu\ (>460\ \text{nm})} \text{n-GaAs}\ (h^+\cdots e^-) \tag{2}$$

to the semiconductor–electrolyte interface would then oxidize 1-vinylpyrene. And as observed in the electrochemical experiments such an oxidation of the monomer induces the cationic radical polymerization at the electrode surface (reaction 3).



(3)

(PVP-3)

The polymer deposit (PVP-3) was thoroughly washed with CH_3CN and dissolved in THF for the optical measurements. The weight-average molecular weight of PVP-3 was 9600. Both PVP-2 and PVP-3 had lower molecular weights than the polymer synthesized with Ziegler–Natta catalyst.

Absorption and Emission Characteristics. The polymer formed by three techniques (solution-phase Ziegler–Natta polymerization (PVP-1); electropolymerization of SnO_2 (PVP-2); and photoelectrochemical polymerization on n-GaAs (PVP-3)) were characterized by recording their absorption and emission spectra in THF solutions. In Figure 3, the absorption spectra of poly(vinylpyrene) prepared by two different methods are compared with

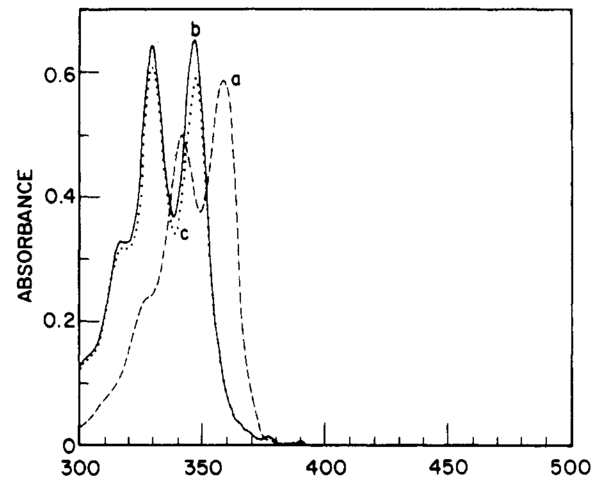


Figure 3. Absorption spectra of (a) 1-vinylpyrene (- - -), (b) PVP-2 (—), and (c) PVP-1 (···) in THF solution.

Table I
Absorption and Emission Characteristics of 1-Vinylpyrene and Poly(1-vinylpyrene)

	$\lambda_{\max}^{\mathrm{abs}}$,[a] nm	$\lambda_{\max}^{\mathrm{em}}$,[a] nm	$\lambda_{\max}^{\mathrm{em}}$,[b] nm	τ_{em},[a] ns
1-vinylpyrene	342, 359	393, 414	490	57 ± 1[c]
PVP-1	330, 347	485	483	113 ± 2[d]
PVP-2	330, 347	485	483	112 ± 2[d]
PVP-3	330, 347	480	470	109 ± 2[d]

[a] In THF. [b] As a film on SnO_2 glass or n-GaAs. [c] Emission monitored at 400 nm. [d] Emission monitored at 480 nm.

1-vinylpyrene in THF. The absorption peaks of the polymer are blue shifted (~10 nm) as compared to the absorption peaks of the monomer. The matching of the absorption spectra of PVP-1 and PVP-2 shows the similarity of the absorption characteristics of the two polymers.

The excitation and emission spectra of 1-vinylpyrene, PVP-1, PVP-2, and PVP-3 are shown in Figure 4. 1-Vinylpyrene in THF exhibited structured fluorescence emission with maxima at 393 and 414 nm. However PVP-1, PVP-2, and PVP-3 in THF exhibited fluorescence emission which was broadened and red shifted ($\lambda_{\max} \sim 485$ nm). This emission which is assigned to the excimer of pyrene is commonly observed in bipyrenyl compounds.[13,14] Though the possibility of the ground-state dimer formation is small in dilute solution, two pyrene units attached to the long C–C chain could partially overlap to induce an excimer emission. Similar excimer emissions of naphthalene and anthracene polymers have also been reported.[15,16] With polymeric anthracene, Hargreaves et al.[15] found that dimerization occurs at the 9,10 positions. Upon blocking these positions with a phenyl, they were able to retard the excimer formation.

1-Vinylpyrene films coated on SnO_2-coated glass exhibited an excimer emission with a maximum around 500 nm (Figure 5) similar to that reported for pyrene adsorbed on different supports in which the probability of overlapping of two pyrene units was quite high.[17] Though the excimer emission of PVP-2 film is slightly blue shifted, as compared to the excimer emission of 1-vinylpyrene film, the broad structureless emission observed with PVP-2 in THF solution and in film confirmed it as an excimer emission.

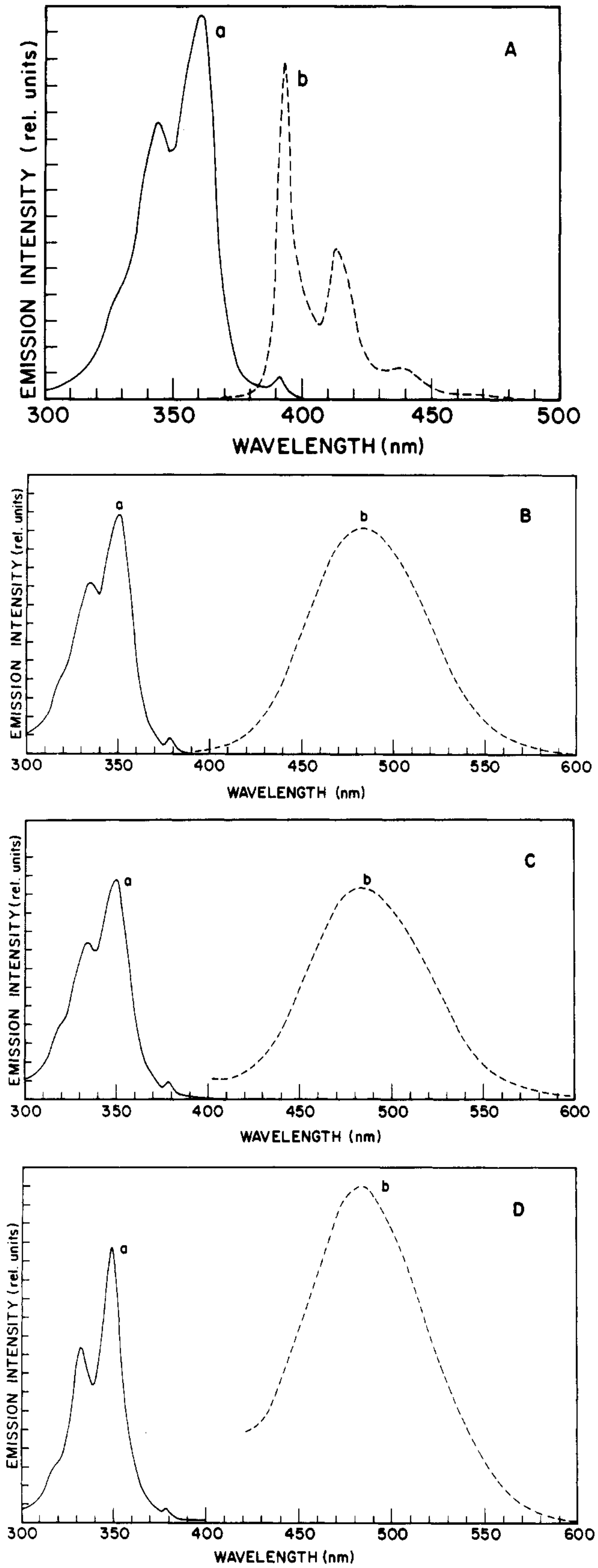


Figure 4. Excitation (a) and emission (b) spectra in THF solution: (A) 1-vinylpyrene (λ^{em} = 410 nm, λ^{ex} = 340 nm); (B) PVP-1 (λ^{em} = 510 nm, λ^{ex} = 340 nm); (C) PVP-2 (λ^{em} = 515 nm, λ^{ex} = 340 nm); and (D) PVP-3 (λ^{em} = 500 nm, λ^{ex} = 340 nm). [The wavelengths in parentheses are the emission and excitation wavelengths employed for monitoring the spectra.]

The emission spectrum of PVP-3, photoelectrochemically coated on n-GaAs, is shown in Figure 6b. The broad excimer emission was similar to that observed for PVP-2 film coated on SnO_2 glass. No such emission could be seen from the bare n-GaAs surface (Figure 6a), if the visible light irradiation was not done during the photoelectrochemical experiment. This established the photocatalytic role of the semiconductor in inducing the polymerization

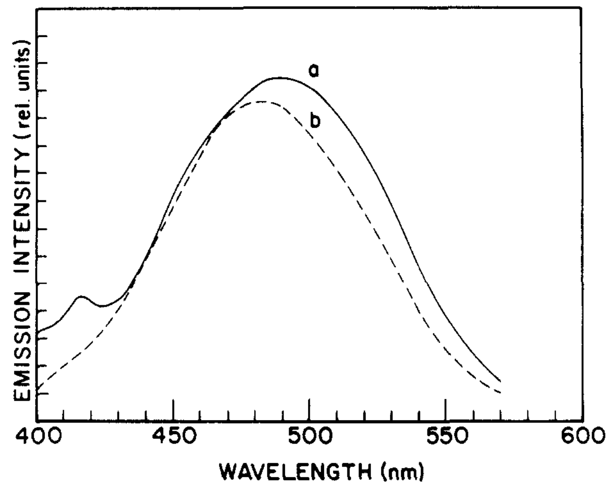


Figure 5. Emission spectra of (a) 1-vinylpyrene and (b) PVP-2 films coated on SnO_2 glass (λ^{ex} = 340 nm).

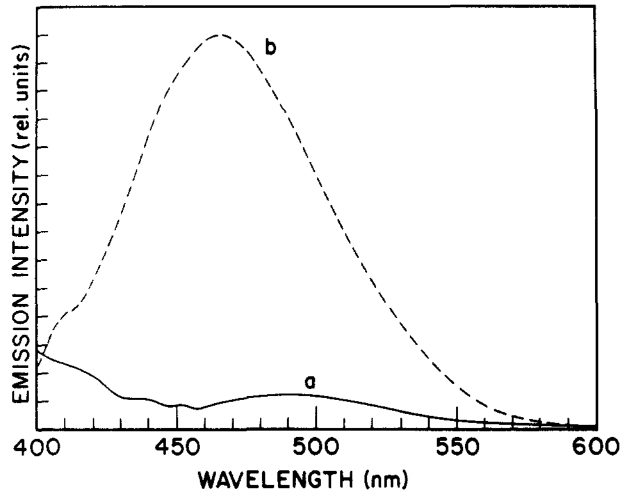


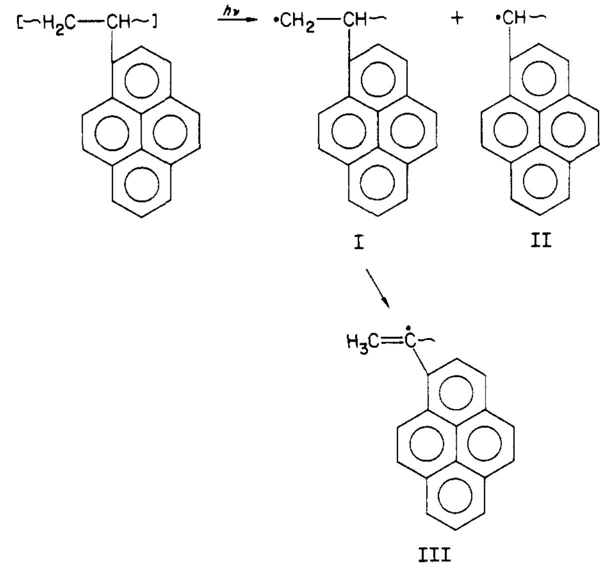
Figure 6. Emission spectra of n-GaAS electrode (with front face measurements) after subjecting it to the photoelectrochemical polymerization conditions (0 V vs. Ag/Ag^+ in acetonitrile containing 1-vinylpyrene): (a) without irradiation and (b) with irradiation of visible light.

of 1-vinylpyrene. This example highlights not only the importance of semiconductors as photocatalysts in photoelectrochemical polymerizations but also the use of similar polymerizations in stabilizing the narrow band gap semiconductors. Application of photoelectrochemically polymerized films in retarding the photocorrosion of the narrow band gap semiconductors is currently being pursued.

Excimer Emission Lifetimes. The lifetimes of the excimer emission of poly(vinylpyrene) prepared by different methods are summarized in Table I. The excimer lifetimes of PVP-2 and PVP-3, 112 and 109 ns, respectively, were close to the lifetime of PVP-1 (113 ns), but varied significantly from the fluorescence lifetime of 1-vinylpyrene (57 ± 1 ns). These values of excimer lifetimes were higher than the value of 87 ns reported for a pyrene excimer in a copolymer of 2-vinylnaphthalene and 3-vinylpyrene in CH_2Cl_2 solution.[9] The nature of the polymer chain motions or interactions within the polymer coil may influence the decay of the excimer emission. The decay of the excimer emission could be fitted to the biexponential decay kinetics. The contribution of the fast component to the emission decay was negligible at lower laser pulse intensities (<0.1 mJ). Similar deviations in the emission decay have been observed for poly(*N*-vinylcarbazole),[18] naphthalene,[19] and anthracene polymers.[15] Excited-state annihilation processes or the presence of dual excimer states would lead to a multiexponential emission decay.

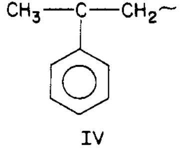
As proposed by Fredrickson and Frank,[20] excimer formation in the aromatic polymers may proceed through a very complex series of energy-transfer steps, intermediate excited-state entities, and/or dynamical processes.

Photodegradation of PVP. Poly(vinylpyrene) was found to photodegrade upon exposure to UV light and electron spin resonance (ESR) experiments were carried out to elucidate the mechanism of photodegradation. The (asymmetric broad) ESR (spectrum) of 77 K UV-irradiated PVP is a superposition of at least two major radicals.[21] As Figure 7a indicates, the ESR spectrum of room-temperature irradiated PVP is basically a four-peak structure. When a 77 K UV-irradiated PVP was heated to room temperature under vacuum, almost 70% of the total radical concentration disappeared. The ESR spectrum of the remaining radicals (Figure 7b) is a four-line structure and resembles that of the sample irradiated at 298 K. The spectra shown in Figure 7 could be assigned to radical III. This radical is believed to be the product of the thermal rearrangement of the energetically less stable radical I or by H abstraction from a neighboring polymer chain by I. Radical I is formed by photolytic chain scission of PVP.



The fairly good resolution of the four-peak ESR spectrum (peak-to-peak line width, ΔH_{pp} = 8.3 G) indicates that the methyl group is relatively free to rotate and that all other possible hyperfine interactions are weak.

Brown et al.[22] observed a four-line ESR spectrum with ΔH_{pp} of 7.8 G in γ-irradiated poly(α-methylstyrene). The spectrum was assigned by these authors to radical IV



IV

formed by main-chain scission of the polymer. The close resemblance between the ESR spectrum of racial IV of γ-irradiated poly(α-methylstyrene)[22] and that of Figure 7 lends support to the suggested radical structure (III).

Conclusion

We have demonstrated two simple techniques for the preparation of the aryl vinyl polymer films on electrode surfaces. The emission characteristics confirmed that the

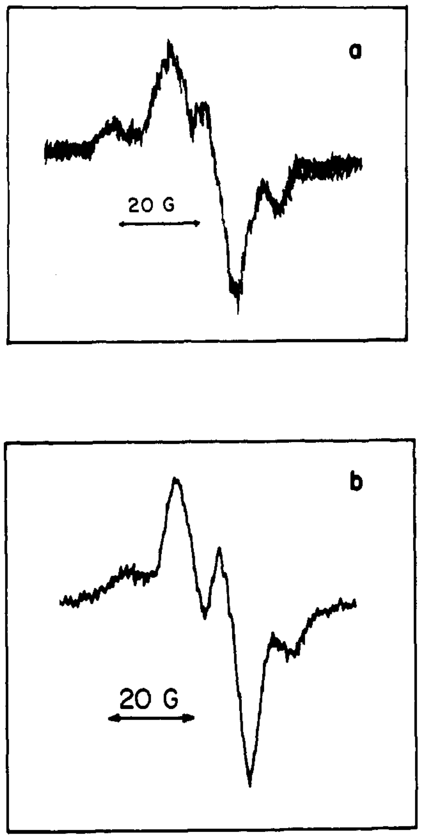


Figure 7. ESR spectra of PVP-1: (a) UV irradiated at 298 K and measured at 77 K; (b) UV irradiated at 77 K, heated to 298 K, and measured at 77 K.

polymers (PVP-2 and PVP-3) produced from electrochemical and photoelectrochemical methods had the characteristics of the polymer (PVP-1) synthesized with Ziegler–Natta catalyst. Visible-light-induced photoelectrochemical polymerization has been reported for the first time at a n-GaAs semiconductor electrode.

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Registry No. Poly(1-vinylpyrene), 25120-43-8; 1-vinylpyrene, 17088-21-0.

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A Soluble Linear Schiff-Base Coordination Polymer Containing Eight-Coordinate Zirconium(IV)

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ABSTRACT: The first soluble linear Schiff-base heavy-metal coordination polymer has been synthesized via the condensation of 1,2,4,5-tetraaminobenzene and tetrakis(salicylaldehydato)zirconium(IV) in dry dimethyl sulfoxide. The (*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-1,2,4,5-tetraaminobenzenato)zirconium(IV) polymer has a number-average molecular weight of up to 4.9×10^4 based on inherent viscosity, gel permeation chromatography, and elemental analysis. Spectral properties of this polymer indicate a structure analogous to the model compound bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV). Thermal characterization of the polymer is also discussed.

Introduction

Linear metal chelate polymers with Schiff-base ligands in which the metal is a part of the polymer backbone[1-5] or is added to a polymeric Schiff base[5-10] are typically insoluble materials. The X-ray study of bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV)[11] shows that two quadridentate Schiff-base ligands on zirconium(IV) are oriented such that a polymeric extension should be distorted from a strictly linear geometry, which might cause intermolecular stacking and intractability, a serious problem in the attempted polymerizations of divalent ions with Schiff-base (and other) bridging ligands.[12] Further-

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