

ELECTROGENERATED CHEMILUMINESCENCE. A CHEMILUMINESCENT POLYMER BASED ON POLY(VINYL-9,10-DIPHENYLANTHRACENE)

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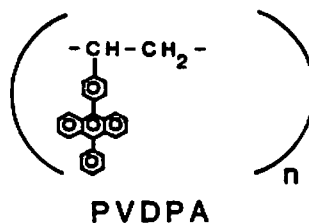
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Received 21 September 1984; in final form 25 February 1985

The electrochemistry, absorption, photoluminescence and electrogenerated chemiluminescence (ECL) of poly(vinyl-9,10-diphenylanthracene) thin films on various substrates in various solvents is described. The electrochemical behavior of the polymer film is very similar to that for 9,10-diphenylanthracene (DPA) in *N,N*-dimethylformamide, indicating that the multiple electroactive groups in the polyvinyl chain do not interact strongly. In situ absorbance measurements of the neutral, oxidized, or reduced polymer films indicate that all of the pendant DPA groups in the chain are electrochemically active during oxidation and reduction. Absorption, photoluminescence, and ECL spectra after potential pulsing or cyclic voltammetric experiments show the presence of components at longer wavelengths than those for the precursor molecules. Such longer wavelength components might be, as in the case of DPA, attributed to the formation of stable products from the decomposition of DPA radical ions.

1. Introduction

We have recently become interested in polymer electrodes [1-4] and in the possibility of producing light emission and studying electron-transfer reactions and charge transfer in polymers by utilizing electrogenerated chemiluminescence (ECL) techniques [5]. Thus, we have recently reported ECL of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy is 2,2'-bipyridine) incorporated into a Nafion polymer film on an electrode surface [1], and ECL of a polymer electrogenerated from tris(4-vinyl-4-methyl-2,2'-bipyridyl)ruthenium(II) [2]. The former was not a regenerative ECL system and involved the irreversible oxidation of oxalate ion in the reaction, while the latter was a regenerative one. Both cases involve initially ionic polymers and a ruthenium(II) system. Our interests extend to the study of aromatic molecules and neutral polymers and the possible effect of conformational changes that can occur during electron transfer in polymers or on absorption and emission. We report here some ECL experiments with a vinyl polymer of 9,10-diphenylanthracene (PVDPA) which was spin-coated on various substrates.



2. Experimental

The polymer (PVDPA) employed in this work was synthesized according to the method of Meyer [6] and was found to have an average molecular weight of 48000 (degree of polymerization 145). A layer of PVDPA about 0.4 μm thick was prepared by spin-coating a 1% PVDPA solution in benzene on the substrate (SnO_2 , Pt or glassy carbon). Tetra-*n*-butylammonium fluoroborate (TBABF_4), polarographic grade (Southwestern Analytical Chemicals, Austin, TX) was twice recrystallized from ethanol, and dried in vacuo at 100°C for two days. Acetonitrile (ACN), spectrophotometric grade (Spectrum Chemical Mfg. Corp., Redondo Beach, CA) was distilled over CaH_2 and stored over molecular sieves. Tetrahydrofuran (THF, reagent grade, Matheson Coleman and Bell)

was distilled over potassium and stored under nitrogen. Propylene carbonate (PC) (Alfa) was refluxed overnight over CaH_2 and then distilled under vacuum ($65\text{--}66^\circ\text{C}$, 0.4 mm Hg); it was stored over molecular sieves under nitrogen.

The cell used for electrochemical and ECL studies was a three-electrode type of conventional design [5,7]. All experiments were performed under nitrogen. The absorption, fluorescence and ECL spectra were monitored by a PAR model 1215 OMA2 optical multichannel analyzer including a silicon intensified target vidicon detector with a vacuum UV scintillator. All electrochemical measurements were performed with the same apparatus and procedures as reported previously [5].

3. Results and discussion

3.1. Electrochemical behavior

As shown in fig. 1A, this polymer is electrochemically active in various solvents (PC, ACN and THF). At a scan rate of 100 mV/s, the anodic peak of a PVDPA film in PC occurs at 1.4 V versus SCE and the cathodic peak at -1.88 V versus SCE; these are close to the potentials for DPA oxidation and reduction in *N,N*-dimethylformamide. This indicates that the multiple electroactive groups in the polyvinyl chain do not interact strongly and behave like the DPA in solution. This behavior is consistent with previous electrochemical results with poly(vinylanthracene), poly(vinylferrocene) and related polymers [3,4,8]. However, the separation of the peak potential ($\Delta E = E_{\text{pc}} \approx 125$ mV), is much greater than 60 mV for both radical anion and radical cation peaks, suggesting that the film is quite resistive to either transport of electrons or electrolyte through the film.

3.2. Absorption spectra

The absorption and fluorescence spectra of PVDPA dissolved in benzene are the same as those of DPA. Similar spectra are observed for a thin film of PVDPA (≈ 0.4 μm) coated on SnO_2 . Little interaction in either the ground or excited singlet states is noted between the chromophores of PVDPA linked by the polyvinyl backbone. The PVDPA film is also very

stable during an extended period of UV irradiation; this is expected for molecules, like DPA, that are resistant to photodimerization and photo-oxidation. Radiative decay is the main relaxation pathway of excited singlet DPA⁺. The absorption spectrum of PVDPA on SnO_2 is shown in curve 1 of fig. 1B and curves 3 and 5 of fig. 1C. The absorption spectra of PVDPA⁺ (curve 4) and PVDPA⁻ (curve 2) generally are the same as the reported spectra for the related DPA species [10]. By comparing the absorption spectra and extinction coefficients (ϵ), we find that PVDPA is totally converted to PVDPA⁺ during electrochemical oxidation, and to PVDPA⁻ on reduction. For DPA, $\epsilon_{380} = 14000 \text{ M}^{-1} \text{ cm}^{-1}$ [9], whereas, for the cation of *p*-methyl-9-phenyl-10-phenylanthracene, $\epsilon_{599} = 14000 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{657} = 13600 \text{ M}^{-1} \text{ cm}^{-1}$ [11]. The absorbances of PVDPA near 380 nm (fig. 1c, curve 3) and PVDPA⁺ near 600 nm (curve 4) are similar. The extinction coefficient for DPA⁻ is not available. However, by comparing the peak currents for the oxidation and the reduction of PVDPA (fig. 1A), we conclude that the conversion of PVDPA to PVDPA⁻ is complete at -1.8 V versus SCE, when the potential is held at this value for a short period (≈ 2 s) and that an $\epsilon_{620} = 4800 \text{ M}^{-1} \text{ cm}^{-1}$ (solution value) can be derived for PVDPA⁻ from curves 1 and 2 of fig. 1B. Even with thicker films (>1 μm), we found total oxidation (or reduction), indicating electrochemical activity extends throughout the whole polymer film. Although the neutral film is stable in PC, ACN and THF for hours, the radical anion and cation forms of PVDPA are both soluble in these solvents. This results in thinning of the film via dissolution and a decrease of peak current during repetitive potential scans. By coating the PVDPA film with another polymer film (Nafion EQ 1100, ≈ 0.2 μm) the dissolution rate was decreased, with only slight modification in the shape of the cyclic voltammograms (the peak current was slightly smaller and ΔE_p slightly larger).

3.3. Photoluminescence and ECL

The fluorescence spectra of PVDPA films have been measured before and after the ECL experiments

† The fluorescence quantum efficiency of DPA approaches unity; see ref. [9].

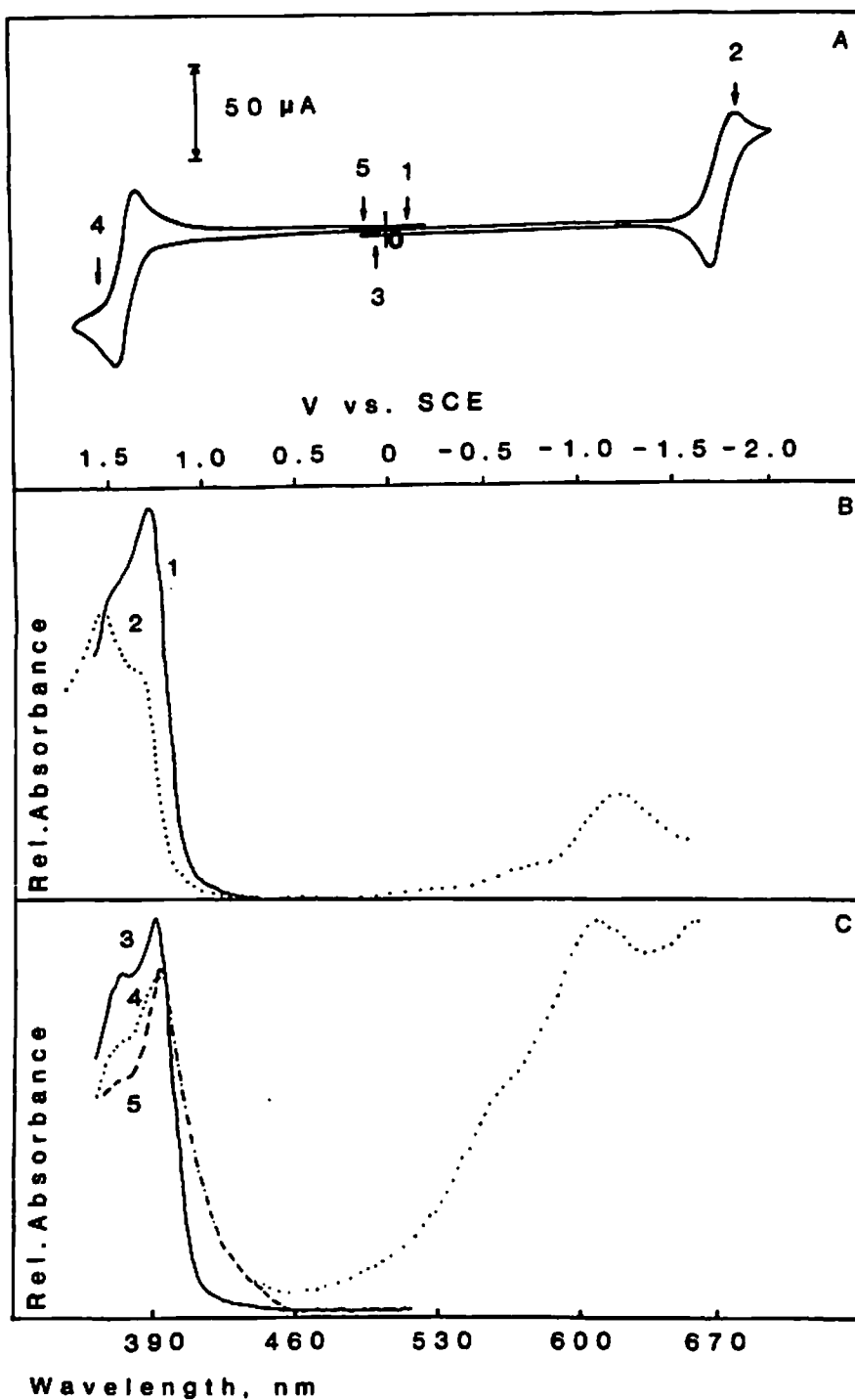


Fig. 1. (A) Cyclic voltammograms in propylene carbonate, 0.2 M TBABF₄ for a SnO₂ electrode coated with a film ($\approx 0.4 \mu\text{m}$) of PVDPA. Scan rate, 100 mV/s. (B) Absorption spectra of a PVDPA film in the same solution as in (A). Curve 1: prior to potential scan (i.e. at position 1); curve 2: potential passes position 2. (C) absorption spectra of a PVDPA film in the same solution as in (A). Curve 3: potential scans back to position 3; curve 4: potential scanning after position 4; curve 5: potential scans back to position 5.

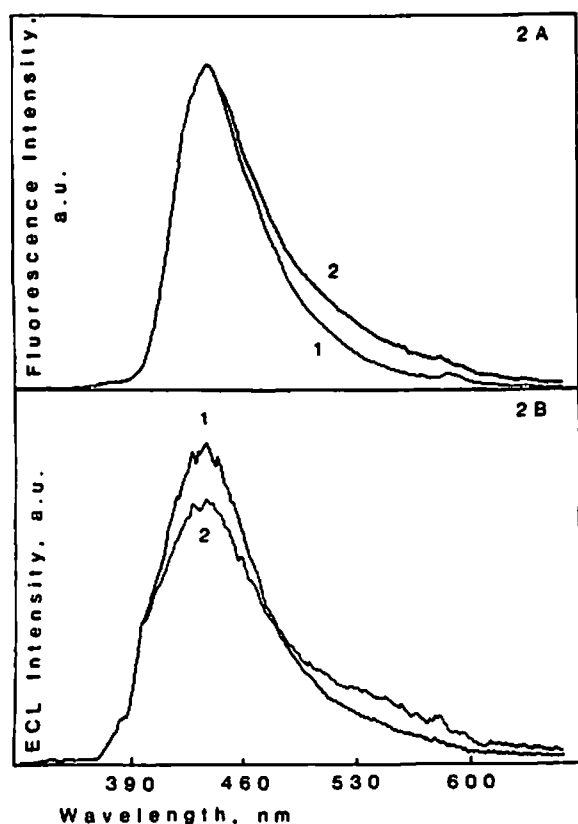
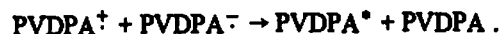
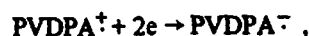
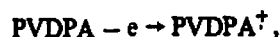


Fig. 2. (A) Fluorescence spectra of a PVDPA film prior to (curve 1) and after (curve 2) ECL experiments. Excitation wavelength 380 nm. (B) ECL spectra of a PVDPA film in PC, 0.2 M TBABF₄. Curve 1: the first 10 cycles; curve 2: the second 10 cycles. Potential step between 1.6 and -2.0 V versus SCE with pulse width of 100 ms.

and are illustrated in fig. 2A. The fluorescence intensity after an ECL experiment (≈ 15 min of continuous pulsing between 1.6 and -2.0 V versus SCE with 100 ms pulse durations) reduced to one-third of the original intensity but is normalized in order to show change in the fluorescence profile after the potential pulsing experiment. Close examination of the fluorescence (curve 2) indicates the appearance of a long-wavelength component. Note that the absorption spectrum of PVDPA films after a cyclic voltammetric experiment (curve 5 of fig. 1C) also shows a long-wavelength tail. These results suggest the formation of a stable product produced by the decomposition of a DPA radical ion [12]. Certain rearrangement of the multichromophores of PVDPA could

also cause the changes in the absorption and emission spectra. Emission occurs upon stepping the potential between 1.6 V (where the electroactive DPA groups are oxidized to the radical cations) and -2.0 V (where the radical anions are formed). The sequence can thus be written (schematically):



As with other similar polymers, charge movement probably involves hopping between the DPA groups [3], with excitation involving anion/cation (or electron/hole) interaction in the polymer film.

ECL spectra (fig. 2B) were recorded with ten cycles of potential steps between 1.6 and -2.0 V versus SCE with 100 ms durations. The first 10 cycles (curve 1) and the subsequent 10 cycles (curve 2) also show slightly different profiles in the ECL spectra. The ECL light intensity decays with time over 5-10 min upon continued cycling, probably because of dissolution of the anionic and cationic forms.

More detailed studies await stabilization of the PVDPA film on the electrodes by derivatization or cross-linking. Stabilization of the film should allow utilization of the ECL technique as a probe to study the electrochemical properties of polymer electrodes.

Acknowledgement

The support of this research by the Army Research Office and the donation of PVDPA from Professor Stephen E. Webber are gratefully acknowledged.

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