Mass and Energy Transport in Conjugated Polymer Langmuir−Blodgett Films: Conductivity, Fluorescence, and UV−Vis Studies

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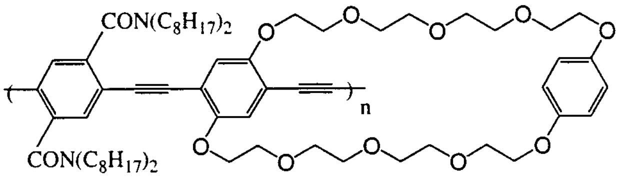
ABSTRACT: We have investigated a model thin film sensory system in which analytes diffuse into multilayers of a fluorescent conjugated polymer. The film thickness is precisely controlled by depositing discrete monolayers by the Langmuir−Blodgett technique. The effects of analyte mass transport and energy migration on the photophysical properties of the films were investigated by conducting UV−vis, fluorescence, and electrical conductivity measurements. Thin films show different properties when compared to relatively thick films due to prevailing surface phenomena. The diffusion constant of the analyte through the films is estimated to be $\sim 7 \times 10^{-14}$ cm^2/s from an analysis of a phenomenological model. A bilayer LB film exposed to the analyte implies higher sensitivity in fluorescence quenching compared to a solution system due to a fast interpolymer energy migration in the condensed phase. However, as the number of layer increases, the efficiency of fluorescence quenching decreases. The difference between a sensory system with emissive surface traps and one with bulk distributed quenching traps is discussed.

Introduction

Fluorescence chemosensors based on conjugated polymers are self-amplifying and display much higher sensitivity than analogous small molecule systems. The self-amplification exhibited by these systems results from effective energy transport along the polymer backbone and between polymer chains.[1−4] Recently, we demonstrated that interpolymer energy migration is an important mechanism for the amplification of sensory signals particularly in solid-state chemosensors.[2] In that study, immobile luminescent traps were placed on the surface of a well-defined multilayer Langmuir−Blodgett (LB) film of a conjugated polymer. A phenomenological model was used to analyze the energy migration and deduce an estimate of the exciton's diffusion length and the excitation hopping rate.[2] However, in most solid-state sensory systems, the analytes will likely diffuse into the film and establish a distribution depending on porosity of a film and specific interactions between a sensory polymer and the analyte. In this case, the polymer's response is expected to be somewhat different from the system with immobile surface traps. Therefore, to determine universal design principles, it is important to study the influence of analyte mass transport and energy migration in a sensory polymer film on the photophysical properties of the sensory film.

In this contribution, we investigate a model system in which a cationic analyte, paraquat (PQ), diffuses into multilayer LB films of a sensory polymer. PQ is an effective fluorescence quencher and forms strong host−guest interactions with the cyclophane-containing polymer **1**, used here.[1] By studying fluorescence quenching, electrical conductivity, and UV−vis spectra of the system, we found that transport properties in the LB films depend considerably on the number of LB layers. Thin two- and four-layer films, in which the structure is different and surface effects are dominant, are dramatically different than relatively thick films with bulk properties. These results are in good agreement with a phenomenological model that takes into account the distribution of the quenching traps (PQ) in the film and fast energy migration along the polymer backbone.



Polymer **1**, Mn=81,200 PDI=3.4

Results and Discussion

UV−vis spectra of a bilayer LB film of polymer **1** treated with different concentrations of PQ solution in acetonitrile are presented in Figure 1a. As the PQ concentration increases, the absorption band shifts to longer wavelengths, and at $C > 8 \times 10^{-5}$ M the band intensity begins to decrease. The decreasing intensity arises from the fact that **1** is gradually dissolved from the film in PQ solutions with higher concentration. This was verified by conducting UV−vis spectroscopy after rinsing the treated samples with pure acetonitrile. This procedure removes deposited PQ and restores the initial shape of the absorption spectra. For samples treated at low PQ concentration ($C < 8 \times 10^{-5}$ M), the spectra of the virgin films were fully recovered, but for $C > 8 \times 10^{-5}$ M the spectral shape returns with a decreased intensity.

Figure 1b shows the differential absorption spectra of a bilayer LB film. The initial UV−vis spectrum (before PQ treatment) was subtracted from the spectra of the LB films treated with varying concentrations of PQ solutions. The appearance of the band at 452 nm

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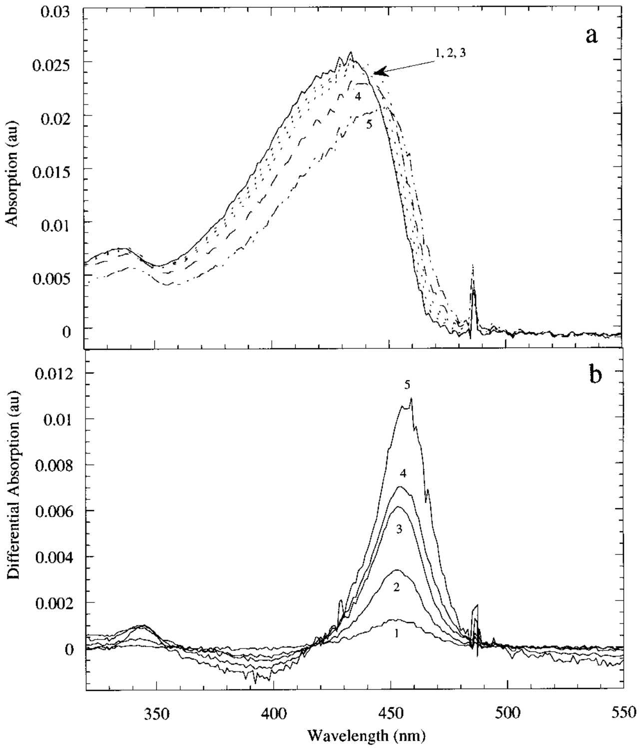

Figure 1. UV–vis spectra of a bilayer LB film of **1** treated with various concentrations of PQ in acetonitrile. (a) Solid line: $C = 0$ M; 1, 2, 3 (dotted lines): $C = 2 \times 10^{-5}$, 4×10^{-5}, 8×10^{-5} M; 4: $C = 2 \times 10^{-4}$ M, 5: $C = 6 \times 10^{-4}$ M. (b) Differential absorption spectra of the same film: normalized initial spectrum (solid line in (a)) was deducted from the spectra of the film treated with PQ. The normalization of intensity was carried out at $\lambda = 415$ nm, where we assume that there is no absorption of the new band.

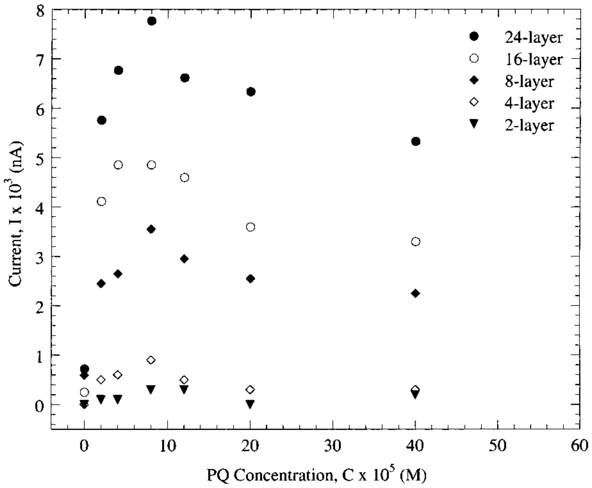

Figure 2. Electrical current (see Experimental Section for details) of multilayer LB films doped with various concentration of PQ solutions. From bottom to top: 2-, 4-, 8-, 16-, and 24-layer LB film.

clearly indicates that PQ binding generates a new excited state with lower energy than that of the pure polymer ($\lambda_{\max} = 432$ nm). The maximum of differential 452 nm absorption band is constant over the range of concentrations and appears to be related to charge-transfer interactions. Previous studies have been performed on PQ showed that it forms a 1:1 molecular inclusion complexes with a bisparaphenylene-34-crown-10 (polymer **1**'s cyclophane) in the solid state as well as in solution.[5] The authors observed a charge-transfer absorption band at 435 nm corresponding to the complex formation in solution.[5c] In the following discussion, we have elucidated that the new excited state acts as an irreversible trap for excitations migrating in the film. The irreversibility comes from the fact that Boltzman factor, $e^{-\Delta E/kT}$, of the system is less than 0.01 at ambient temperature. The energy, ΔE, is the difference between the excitation energy and trap energy which are the difference of their absorptions (approximately 0.127 eV). Figure 1b shows that band intensity and consequently amount of bound PQ in the film increase with increasing PQ concentration.

We also carried out conductivity measurements on our LB films treated with PQ solutions (see Experimental Section). Figure 2 shows the electrical currents of various multilayer LB films treated with different concentration PQ solutions. All of the data were collected after dipping the LB films into PQ solutions for 20 s. We observed that increasing dipping time leads to an increase of signal intensity for all films except two- and four-layer films. This indicates that, for the films with more than eight layers, 20 s is not long enough for PQ molecules to penetrate down to the very bottom layer to saturate the film. Thicker films display stronger signals, thereby indicating the penetration of PQ molecules into a film. The binding constants of PQ with the polymer and the diffusion constant will determine the amount of PQ absorbed into the film. As we observed in UV–vis spectra, we found a decrease of the current of the film treated with PQ solution at $C > 8 \times 10^{-5}$ M, again due to the polymer's increased solubility under those conditions. The current was less than 10^{-3} nA (background level) for a fresh film after dipping into pure acetonitrile or for a sample previously treated with PQ that was rinsed with pure acetonitrile three times. From these measurements, the conductivity of undoped pure polymer **1** is determined to be less than 5×10^{-11} $(\Omega\ \text{cm})^{-1}$ for a LB bilayer, indicating a high purity for **1**. For comparison, a conductivity of 5×10^{-16} $(\Omega\ \text{cm})^{-1}$ was found in a pure film of a PPV–ether derivatives.[6] Therefore, the conductivity of LB films treated with PQ solutions must come from the mobility of holes released by the capture of electrons by the bound PQ molecules. The binding sites are most likely the electron-rich macrocycles of the polymer that have an association constant of 1300 M^{-1} in solution. However, in a solid film, PQ binding may also occur near macrocycles.[5]

The dependence of the charged complex absorption peak's intensity on the number of LB layer at a PQ concentration of $C = 2 \times 10^{-5}$ M is shown in Figure 3 (open circles). The dependence of current with an applied voltage of 2 V on the number of LB layers at the same concentration of PQ solution is also shown in Figure 3 (full circles). Note that the data for the thinner two- and four-layer films deviate from other data. We attribute this deviation to a prevalence of surface phenomena. The rather high value of UV–vis signal for the thin films can be explained by a strong PQ binding to the surface. The specific morphology of the LB bilayer should also play an important role. The first layer was deposited on a hydrophobic surface with a downstroke, and all subsequent layers were deposited with an upstroke. Hence, the bottom two layers have distinct structure with the macrocycles of each layer facing each other in a head-to-head arrangement.[7] All other layers have the macrocycles pointing toward the surface, and a head-to-tail registry exists between layers.[7] The electric current measurements for the thin films also

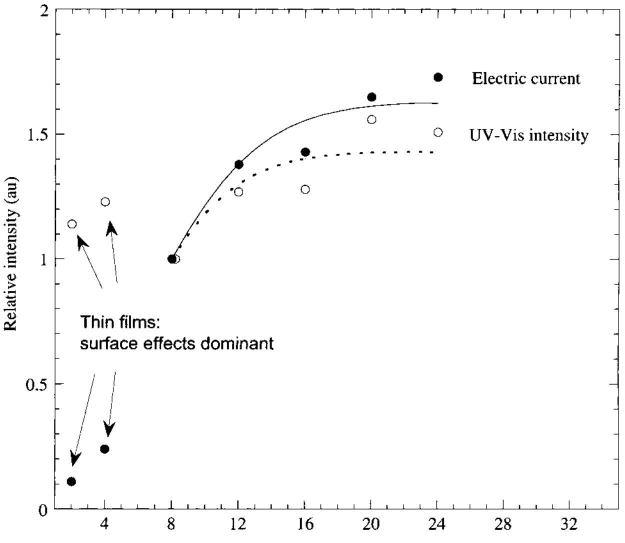

Figure 3. Relative intensity of the UV−vis spectra of the new band at 452 nm and electrical current as a function of the number of LB layers. Films were treated with a PQ solution at 2 × 10^{-5} M. Relative intensities were calculated relative to a eight-layer film. The curves are the best fit for the experimental data. Experimental errors for the current data were less than ±15%. UV−vis data have experimental errors less than ±25%.

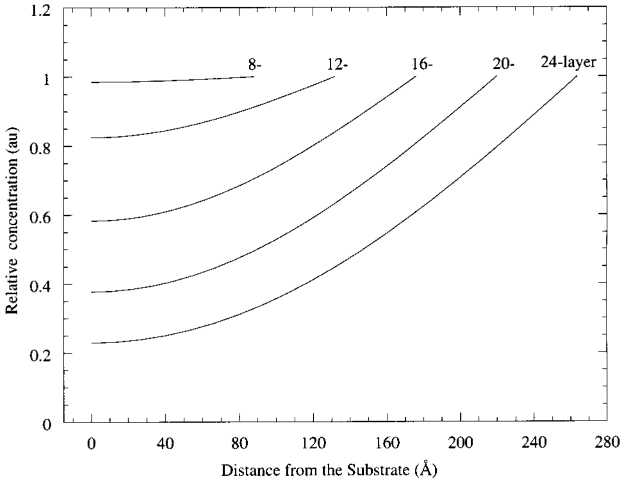

Figure 4. Relative concentration profile of absorbed PQ distribution ($C_f(x,t)/C_0$) in various number of LB films. The plots were produced with the eq 2 at $t = 20$ s and $D = 7 \times 10^{-14}$ cm²/s. The thickness of each layer of multilayer LB films of **1** was estimated to be 11 Å.[7]

showed considerably smaller values than the thicker films. We postulate that the surface phenomena here again is responsible for the low current. It is well-known fact that a solid−air interface is an effective trap for mobile charges.[8]

As the film thickness increases, for films of eight layers or more the UV−vis intensity at 452 nm and the electric current show a consistent increase, presumably due to a transition from surface to bulk properties. For a quantitative interpretation of the results, we applied a simple Fickian diffusion model. As was mentioned, PQ distribution within thick films is a consequence of bulk diffusion. Since the experiments were conducted at room temperature, above **1**'s T_g of −2 °C, bulk diffusion should be facile.[9,10] Moreover, the specific structure and organization of **1** provide for a relatively large distance between polymer chains since the head-to-tail organization of the macrocycles and the bulky dialkylamide side chains keep the polymers apart and prevent $\pi-\pi$ aggregation.[7,11] For simplicity, we assume that diffusion coefficient is constant and PQ binding with **1** is reversible with a thermodynamic equilibrium between bound (immobilized) and freely diffusing molecules. Our analysis focuses on bound PQ, which is responsible for the new UV−vis band and the increase in conductivity. The measured signal S (the new UV−vis band and the electric current) can be expressed as $S \sim \int_0^d C_b(x,t)\,dx$, where d is the film thickness, and $C_b(x,t)$ is the concentration of bound molecules at time t and distance x from the surface. According to an established result,[12,13] if $C_f(x,t) = RC_b(x,t)$, the diffusion equation for a reversible reaction becomes

$$\frac{\partial C_f(x,t)}{\partial t} = \frac{D}{R+1}\frac{\partial^2 C_f(x,t)}{\partial x^2} \tag{1}$$

where $C_f(x,t)$ is concentration of free diffusing molecules, D is a diffusion constant, and R is the constant defining the ratio between bound and free species. The amount of PQ in solution is high enough compared to absorbed PQ in a film, so C_0, the PQ concentration at the film surface, is reasonably assumed as a constant. The solution of eq 1 for the experimental conditions of diffusion through a plane sheet with one impermeable surface (glass slide in our case) and the other surface maintained at constant concentration C_0 is given as[13]

$$C_f(x,t) = C_0 - \frac{4C_0}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}e^{[-D(2n+1)^2\pi^2 t]/[4(R+1)d^2]}\cos\frac{(2n+1)\pi x}{2d} \tag{2}$$

Integration of eq 2 over a film thickness provides the S value, which was used for comparison with experimental data. Data fitting was conducted for the LB films thicker than four layers by using the adjustable parameters $D/(R+1)$, a scaling cofactor at the fixed time t, and the film thickness d. We determined $D/(R+1)$ values of 8×10^{-14} and 6×10^{-14} cm²/s for the current and UV−vis data, respectively. However, we could not perform a reasonable fit of the two- and four-layer films. This result is consistent with our previously described understanding that surface phenomena and a different structure produce different behavior in the thin films. The upper limit of the PQ diffusion coefficient can be estimated at approximately 7×10^{-14} cm²/s. This is a reasonable magnitude when compared to literature values of diffusion coefficients for organic molecules in polymer films.[10,13,14] The computed concentration profiles, $C_f(x,t)/C_0$, at $t = 20$ s with $D = 7 \times 10^{-14}$ cm²/s for the films with varying number of layers are shown in Figure 4. Even though this model has a number of limitations, for example, it excludes any consideration of a concentration-dependent diffusion coefficient and non-Fickian diffusion,[15] we found a satisfactory agreement with the experimental data.

Fluorescence studies were conducted to interrogate energy transport in multilayer LB films. PQ is a very effective fluorescence quencher for **1**.[1] In a solid film, wherein efficient intermolecular energy transfer occurs in addition to energy migration along a polymer backbone, we can expect a much more facilitated fluorescence quenching of **1** by PQ.[2] Excitations in a condensed

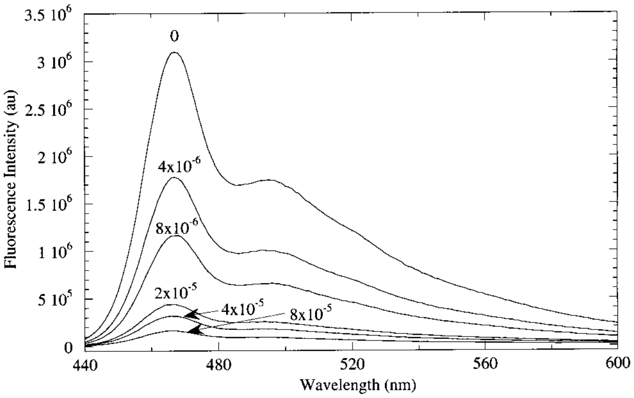

Figure 5. Fluorescence spectra of 16-layer LB film of **1** treated with various concentration of PQ solution in acetonitrile.

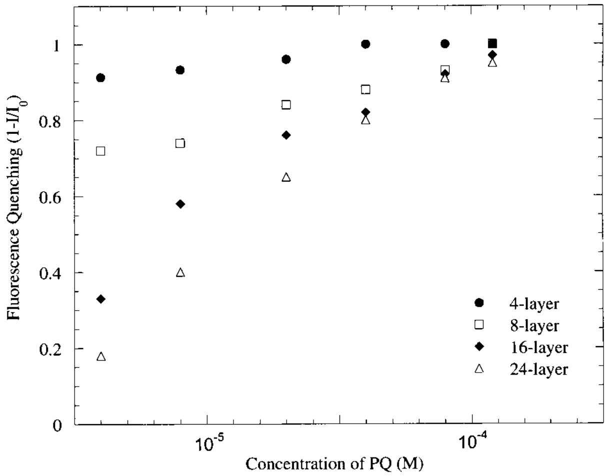

Figure 6. Fluorescence quenching Q ($1 - I/I_0$) of LB films as a function of PQ concentration in acetonitrile. Experimental errors were less than ±10%.

phase perform 2-D and/or 3-D random walks, visiting more new sites as compared to isolated polymer chains with a quasi-1-D geometry.[16] In addition, the alignment of the polymer main chains (transition dipole moments) which we have previously shown for **1** when deposited by the LB technique should increase the Förster energy transfer effieciency.[2] Comparisons of the quenching efficiency between in the solution and in the LB films qualitatively support our expectation. In previous solution studies the quenching, Q, was 78% when the molar concentration of PQ is 3.56×10^{-5} M ($Q = 1 - I/I_0$, where I_0 and I are fluorescence intensity without and with PQ, respectively).[1] Whereas, for a bilayer LB film we found that $Q = 93\%$ at a PQ concentration of 4.00×10^{-6} M. Therefore, we observe higher quenching although the concentration of PQ was approximately 1 order of magnitude less than the solution case. This difference cannot be induced by only different binding characters of PQ on the film but must also be related to the fast transport of excitons in highly aligned films. Fluorescence spectra of a 16-layer LB film of **1** treated with increasing concentrations of PQ in acetonitrile are shown in Figure 5.

Figure 6 shows quenching, Q, of four different thickness LB films treated with varying concentrations of PQ. Increases in thickness leads to a decrease of the quenching efficiency. Initially the result appeared contradictory to our previous results, where diffusion length of excitations, migrating along the Z direction (film thickness direction), exceeded 10 LB layers of **1**.[2] Therefore, an increase of number of layers was expected to facilitate energy migration and consequently more efficient fluorescence quenching due to the transition from a 2D to a 3D geometry. However here, we have to consider the difference between immobilized emissive surface traps and quenching traps distributed in a film. Even though the length of excitations exceeds 10 LB layers, only a fraction of the excitations from remote layers reach the emissive surface traps. As the distance increases, the fraction reaching the surface decreases. In the case of emissive surface traps, within the long-range limit of the excitation migration distance, emission from surface traps increases due to the energy transfer from the remote layers.[2] However, quenching traps especially distributed within a film creates a different situation. Using our previous result that intralayer energy migration is much faster than interlayer migration[2] and the quenching trap distribution profiles (Figure 4), we can explain the lowering quenching efficiency as the number of layer increases. The concentration of traps in remote layers (closer to the substrate) is much lower than it is at the surface. Therefore, while the layers close to the surface lose fluorescence due to a fast intralayer energy migration, remote layers are not effectively quenched. In a thick film the portion of layers with relatively low trap concentrations prevail, and the quenching efficiency decreases with increasing numbers of layers. In addition, it should be noted that in our previous experiment the energy migration parameters for the direction normal to the surface were obtained exclusively with immobile surface traps. Unlike the case of emissive traps wherein direct Förster energy transfer can occur from remote layers, the quenching PQ traps likely function by electron transfer, thereby reducing the efficiency of long-range energy transfer.

In summary, we have investigated mass and energy transport in sensory LB films by conducting UV−vis, fluorescence, and electric conductivity measurements. The diffusion coefficient of a quenching trap into a sensory film is rather low, $\sim 7 \times 10^{-14}$ cm^2/s. Unlike the case of emissive surface traps, the sensitivity of sensory LB films to a quenching trap distributed within a film decreases as the number of layer increases. This result is due to a fast intralayer energy migration and less effective long-range energy migration. The results of this study provide important insights for the improved designs of fluorescence quenching-based sensory films.

Experimental Section

A detailed investigation of the Langmuir−Blodgett deposition of polymer **1** and the determination of film thickness was reported elsewhere.[7] The LB films are transferred from the air−water interface to substrates at the surface pressure of 18 mN/m. Films were deposited on hydophobic substrates. Paraquart (PQ) was obtained from Aldrich Chemical Co. and used without purification. The PQ-treated LB films were prepared by dipping LB films into PQ solutions in acetonitrile at concentrations varying from 2×10^{-6} to 6×10^{-4} M for 20 s followed by drying. UV−vis spectra were obtained from a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescence studies were conducted with a SPEX Fluorolog-τ2 fluorometer (model FL112, 450 W xenon lamp) equipped with a model 1935B polarization kit. Fluorescence spectra of the LB films were recorded in front-face (22.5°) detection mode. All emission and excitation spectra were corrected for the detector response and the lamp output. For electrical current measurements, LB films were coated on electrodes (Abtech Co.)

with 50 interdigitated microelectrode pairs: digit length = 4985 μm, digit width and interdigit space = 5 μm, digit height = 0.25 μm. Electrical current measurements (dc current) were carried out in an evacuated box in an ambient atmosphere with a PGSTAT-20 potentiostat (Echo Chemie Autolab). The current was measured at 3 min after application of the voltage of 2 V to get a stabilized value. The current of the sample treated with pure acetonitrile was used as a reference before each measurement with PQ solution treatment. The conductivity was calculated from the geometry of the interdigitated electrode and the thickness of a LB bilayer.[7] The numerical solutions were obtained using the NAG program (FORTRAN library), which was developed in part by one of the authors (I.A.L.) at the Ukraine Academy of Sciences; however, the same solutions may be obtained by any mathematical program capable of numerical summation and integration.

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