Fluorescence Decays in Aromatic Polymers: Analysis of Kinetic Models and Their Identifiability and Distinguishability

K. Sienicki* and G. Durocher

Département de Chimie, Université de Montréal, C.P. 6128, Succ. A, Montréal, Québec, H3C 3J7, Canada

Received May 7, 1990; Revised Manuscript Received August 1, 1990

ABSTRACT: Fluorescence decay profiles of aromatic polymers have a complex character, and several models have been put forward to account for their complexity. We have examined the uniqueness of the models proposed by different authors using a deterministic approach to the identifiability and distinguishability of first-order photophysical reactions. Identifiability deals with the problem of determining whether a photophysical experiment is able to give sufficient information on the parameters of a proposed kinetic model. By investigating indistinguishability, one can generate a number of models that give the exact same values of the photophysical observables. It has been shown that only under very special circumstances the models explaining fluorescence decay profiles of aromatic polymers can be regarded as uniquely identifiable and distinguishable. Several models that are indistinguishable from a given one have been discussed.

I. Introduction

In recent years there has been a substantial progress in understanding photophysical and photochemical properties of aromatic polymers.[1] A large number of various photophysical properties of aromatic polymers were collected and related to their structure and dynamics.

Extensive studies have been reported regarding interpretation of fluorescence decay profiles from many aromatic polymers and their copolymers.[1] The summary of models proposed by different authors to interpret decay curves of aromatic macromolecules is shown in Table I. The first model (I) is a classical two-state kinetics[2] for monomer–excimer formation in the solution, and we shall call this type of kinetics a Birks model. It was shown[1,2] that, under the assumption of time-independent rate constant for excimer formation, the Birks model does describe correctly the decay profiles from aromatic polymers. However, recently it has been shown that in some cases the transient part of the rate coefficient is important in the analysis of monomer–excimer kinetics for small aromatic molecules[3,4] as well as polymers.[5-9]

Models II and III were proposed by Phillips et al.[10] to explain fluorescence profiles of polymers and copolymers of vinylnaphthalene, naphthyl methyacrylate, acenaphthene, and styrene. Those models were proposed as a result of the observation that fluorescence decay profiles from the mentioned macromolecules cannot be described by model I and monomer–excimer fluorescence is described adequately by three exponential functions. In models II and III excimer E* can be populated from monomer states M_2^* and M_1^*. Monomer state M_1^* represents a chromophore that is in kinetic (spatial) isolation from the normal distribution of monomer states M_1^*. Model IV was proposed by Kauffmann et al.[7] as the result of studies of poly(*N*-vinylcarbazole). Model IV proposes two class of monomer states: $\{X_1^*\}$ represents a density of state distribution transport states, which deliver excitation to a small ensemble of energy-relaxed monomeric chromophores, $\{X_2^*\}$. Excimer $\{X_3^*\}$ is formed by rotational motion of adjacent chromophores to the $\{X_2^*\}$. In the original formulation, a perturbative method was used to calculate respective fluorescence profiles, assuming a time-dependent rate coefficient for energy migration between monomer states $\{X_1^*\}$. Later on, one of us[4] presented a simple and an exact method of calculation of fluorescence decays of model IV, assuming a time-dependent rate coefficient of energy migration and excimer formation. Models V–VII were proposed by Holden and Guillet,[11] De Schryver et al.,[12] and Phillips et al.[13] Those models contrary to model IV were interpreted by assuming multiexponential fluorescence decay profiles. At the same time on the basis of classical photophysical studies of energy migration and energy transfer, several authors[5-8] were arguing that regardless of the model the process of energy migration between monomer states should lead to nonexponential fluorescence decays. However, this behavior of fluorescence decays was not reported experimentally. Recently, on the basis of numerical[4] and experimental[3] investigations, it was shown that in many situations time-dependent kinetics can be well approximated by two exponential functions. In the case of the Birks model (model I in Table I), it was shown that, as the rate constant of excimer dissociation increases, the difference between time-dependent and time-independent kinetics becomes very small.[4] It was concluded that one can observe good double-exponential fit at high temperature where an efficient process of excimer dissociation is expected. As one slows down excimer dissociation by decreasing the temperature, the fit to double-exponential function becomes worse and worse. This peculiar behavior appears to be characteristic of many photophysical situations.[14] Summing up the above remarks, one can see that time-dependent rate constants for the process of energy migration in polymers could be more common than was previously assumed. There exist two possibilities to justify time dependence of rate constants for energy migration in aromatic polymers. If the number of hops of excitation during its energy migration is large, one can solve kinetic differential equations with an average rate coefficient in the form of $k(t) = a + bt^{-1/2}$.[5-8] The second approach recently proposed is based on calculation of the ensemble average over the distribution of monomer chromophores, assuming a rate constant as predicted by Förster or Dexter for resonance or exchange interactions between chromophores.[15] It is important to notice that in both cases one can obtain an equation for monomer as well as excimer decay in nonexponential form. We shall address this problem in more detail in the next part of the paper.

In spite of still open questions about the satisfactory description of excitation kinetics in aromatic polymers, the problem of identifiability and distinguishability of the

0024-9297/91/2224-1102$02.50/0

Table I
Photophysical Models Proposed To Explain Fluorescence Decay Profiles from Aromatic Polymers

no.	model	ref	no.	model	ref
I	$M^* \rightleftarrows E^*$	1	V	$M_2^* \rightleftarrows M_1^* \rightleftarrows E^*$	11
II	$M_2^* \rightarrow M_1^* \rightleftarrows E^*$	10	VI	$M_2^* \rightleftarrows M_1^* \rightarrow E^*$	12
III	$M_1^* \rightleftarrows E^* \rightarrow M_2^*$	10	VII	$M^* \rightleftarrows E_1^* \rightleftarrows E_2^*$ $\downarrow$ E_3	13
IV	$\{X_1^*\} \rightarrow \{X_2^*\} \rightleftarrows \{X_3^*\}$	7, 9			

proposed models was not yet addressed.[16,17] We have recently analyzed the probem of identifiability and distinguishability of first-order photophysical reactions for monomer–excimer and/or monomer–exciplex kinetics in solution.[18] One can easily show that for example double-exponential decay of fluorescence can be explained by very different kinetic models. In this situation, one has to be able to distinguish these models that lead to the same decay function. At the same moment one can address the question of identifiability of different monomer as well as excimer states (Table I) by using time-resolved fluorescence spectra. In many respects the concern expressed above regarding fluorescence data is very much connected to the problems arising in the interpretation of first-order and/or pseudo-first-order kinetics of chemical reactions, compartmental modeling, and automatic control.[16,17] The problem of uniqueness of parameters leading to the identifiability and distinguishability of various models has been investigated in a number of papers.[16-18] It was shown that it is possible to formulate a rigorous mathematical analysis in order to check the uniqueness of the model that can explain experimental data.

In this paper we shall investigate the identifiability and distinguishability of photophysical models collected in Table I. Also we shall formulate a general model of energy migration and trapping in aromatic polymers, assuming a time-dependent rate coefficient for photophysical processes.

II. Theoretical Preliminaries

A. Identifiability and Distinguishability. We mentioned in the Introduction that two important properties as *identifiability* and *distinguishability* of the proposed kinetic model have to be carefully investigated before deriving a final conclusion regarding the interpretation of experimental data. In this section we shall briefly review some theoretical approaches applied in the problem of interpretation of kinetic data.[17,18] Two basic criteria of interpretation of first-order kinetics have been developed. The first criterion of *identifiability* gives the answer to the problem of determining whether an experiment is able to give the desired information on the kinetic parameters on an assumed model. The second criterion of *distinguishability* gives the answers to the number of models that can generate the same values for the observed quantities in any possible experiment.

Let us first examine the problem of identifiability. A first-order reaction scheme can be described by the kinetic equations in the general form[17]

$$d\mathbf{X}(t,k)/dt = \mathbf{A}(k)\mathbf{X}(t,k) \tag{2.1}$$

with the initial conditions

$$\mathbf{X}(0,k) = \mathbf{X}_0(k) = [\mathbf{X}_0^{(1)}, \mathbf{X}_0^{(2)}(k)] \tag{2.2}$$

where $\mathbf{X}(t,k)$ is the n vector, depending on the p vector $k \in \Omega$ of unknown parameters, which are in our case rate constants and respective lifetimes. The initial conditions (eq 2.2) are specified in a way that the initial concentration vector, $\mathbf{X}_0(k)$, is divided into components $\mathbf{X}_0^{(1)}$, selected to define an experiment, and those in $\mathbf{X}_0^{(2)}(k)$, which are depending on unknown parameters. The system of equations (2.1) is directly related to the response function, $y(t,k)$, in the form

$$\mathbf{y}(t,k) = Z\mathbf{C}(k)\,\mathbf{X}(t,k) \tag{2.3}$$

where $\mathbf{y}(t,k)$ is the m vector of observable quantities, $\mathbf{C}(k)$ is the observation matrix, and Z is the instrumental function.

Let $\tilde{\mathbf{y}}(t)$ represent the response function observed over some time interval T for a kinetic experiment with initial conditions $\mathbf{X}_0^{(1)}$. If there exists a nominal parameter value $k \in \Omega$ such that $\mathbf{y}(t,k) = \tilde{\mathbf{y}}(t)$ can be observed over $t \in T$, then the two parameter values k and $\tilde{k} \neq k$ are indistinguishable in the experiment under consideration if

$$\mathbf{y}(t,\tilde{k}) = \mathbf{y}(t,k) \tag{2.4}$$

for any $t \in T$. Equation 2.4 is the basis for the analysis of identifiability of first-order kinetic reactions, and this equation leads to three distinct situations: (1) if the formal solution $\tilde{k} = k$ of eq 2.4 is unique, the kinetic model, eqs 2.1 and 2.3, is said to be *uniquely identifiable* at $k \in \Omega$; (2) if there exists at most a finite number of distinct solutions $\tilde{k} \neq k$, the kinetic model is said to be *identifiable* at k; (3) for an infinite number of formal solutions of eq 2.4, the kinetic model is said to be *unidentifiable*.

One of the most simple and especially suited methods for analysis of spectroscopic data is the Laplace transform approach.[16,17] Taking the Laplace transform of eqs 2.1 and 2.3, one can obtain

$$\mathbf{Y}(s,k) = Z\mathbf{C}(k)\,[s\mathbf{I} - \mathbf{A}(k)]^{-1}\,\mathbf{X}_0(k) \tag{2.5}$$

where s is the complex argument of the Laplace transformation of the response function, $y(t,k)$.

Definition 2.4 can be extended into Laplace space, and

$$\mathbf{Y}(s,\tilde{k}) = \mathbf{Y}(s,k) \tag{2.6}$$

for $s \in C$, where C is the field of complex numbers and each component $Y_i(s,k)$ for $i = 1, \ldots, m$ of the m vector $\mathbf{Y}(s,k)$ can be expressed by a rational function in the form

$$\mathbf{Y}_i(s,k) = (\Phi_{n+1}{}^i + \ldots + \Phi_{2n}{}^i)/(s^n + \Phi_i s^{n-1} + \Phi_n{}^i) \tag{2.7}$$

where the coefficients $\Phi_j{}^i \equiv \Phi_j{}^i(k,\mathbf{X}_0^{(1)})$. One can define the vector Φ, which is formed by *all* different coefficients in $Y_1(s,k), \ldots, Y_m(s,k)$. Thus the problem of identifiability is reduced to determining the number of solutions of the equation

$$\Phi(\tilde{k}) = \Phi(k) \tag{2.8}$$

We shall show in the next section the practical implementation of the above analysis. Now we shall briefly discuss the problem of distinguishability of first-order reaction kinetics.

Let us assume that we have two reaction schemes denoted by S and $\tilde{S}$, respectively. $\mathbf{y}(t,k)$ and $\tilde{\mathbf{y}}(t,\tilde{k})$ are response functions of the respective reaction schemes with the initial conditions $\mathbf{X}_0^{(1)} = \mathbf{X}_0^{(1)}$ and parameters $k \in \Omega$ and $\tilde{k} \in \tilde{\Omega}$. The two reaction schemes are *indistinguishable* if for any $k \in \Omega$ there exists a parameter $\tilde{k} \in \tilde{\Omega}$ such that

$$\tilde{\mathbf{y}}(t,\tilde{k}) = \mathbf{y}(t,k) \tag{2.9}$$

and vice versa for all $t \in T$. By analogy to the problem of identifiability, one can consider the formal solutions of the polynomial equation[17]

$$\tilde{\Phi}(\tilde{k}) = \Phi(k) \tag{2.10}$$

and calculate formal solutions of eq 2.10 both for $\tilde{k}$ in terms of k and for k in terms of $\tilde{k}$. It is said that the kinetic models are *indistinguishable* if and only if both solutions exist at almost every $k \in \Omega$ and $\tilde{k} \in \tilde{\Omega}$, respectively.[17]

In the next section we shall use the above considerations to analyze identifiability and distinguishability of models presented in Table I.

B. Kinetic Modeling. Photophysical models presented in Table I can be analyzed by assuming first-order kinetics, and one can obtain multiexponential fluorescence decay profiles. Their identifiability and distinguishability we shall analyze in the next section. At this point we shall develop a general model of excitation migration and trapping in aromatic polymers assuming the models presented in Scheme I. This model is a simple generalization of models shown in Table I. One important feature has been added to the model by assuming that excimer dissociation is time dependent. In the classical literature it has been assumed that excimer dissociation is an intramolecular process and therefore it should be time independent.[2] Certainly, this could be the case of excimer formation and dissociation of aromatic molecules in solution where the solute–solute interaction is not strong. However, recently several authors have analyzed reversible dissociation reactions showing that the process of dissociation is described by a distribution of waiting times (time-dependent rate coefficient) rather than by a single dissociation rate constant.[19] The extent of the non-Markoffian contribution to dissociation is related to vibrational relaxation of the excimer. There is no experimental evidence for time-dependent excimer dissociation in aromatic polymers even if it might be possible that strong interactions of chromophores with polymer chain may lead to non-Markoffian dissociation. In the following calculations we shall assume that excimer dissociation is time dependent; however, one can eliminate non-Markoffian dissociation, assuming time-independent rate constant.

The decay responses of each species M_1, M_2, and E subsequent to instantaneous δ-pulse excitation can be expressed by relations

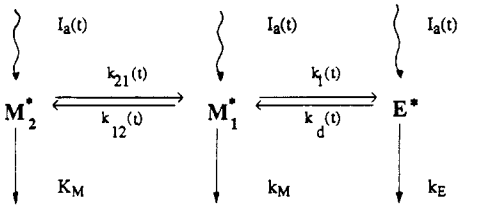
$$f_{M_1}(t) = f_{M_1}(0) \exp\{-k_M t - \int_0^t [k_1(t') + k_{12}(t')]\, dt'\} \tag{2.11}$$

$$f_{M_2}(t) = f_{M_2}(0) \exp\{-k_M t - \int_0^t k_{21}(t')\, dt'\} \tag{2.12}$$

$$f_E(t) = f_E(0) \exp\{-k_E t - \int_0^t k_d(t')\, dt'\} \tag{2.13}$$

where k_M and k_E are rate constants for monomer and excimer fluorescence, respectively. The initial concentrations fulfill normalization relation $f_E(0) = 1 - f_{M_1}(0) - f_{M_2}(0)$. Additionally we have assumed that $k_{M_1} = k_{M_2} \equiv k_M$.

Scheme I



The following derivation of respective fluorescence profiles is in many respects similar to those presented before.[9] Therefore, we shall present only those calculations that are different from the previous one. After direct excitation of the system with rate constant $I_a(t)$, the concentration of excited species could be expressed as a convolution integral between excitation pulse and respective response functions given by eqs 2.11–2.13 and

$$M_1^{(1)}(t) = I_a(t) \otimes f_{M_1}(t) \tag{2.14}$$

$$M_2^{(1)}(t) = I_a(t) \otimes f_{M_2}(t) \tag{2.15}$$

$$E^{(1)}(t) = I_a(t) \otimes f_E(t) \tag{2.16}$$

Let us consider the time evolution of monomer state M_2. Excitation energy $M_2^{(1)}(t)$ can migrate to monomer state M_1, and after (or before) excimer formation and dissociation can return from M_1 to M_2. Thus the concentration of excited monomer M_2 after first return of excitation energy is

$$\begin{aligned} M_2^{(1)}(t) = M_2^{(1)}(t) \otimes \{&k_{21}(t)\, f_{M_2}(t) + k_{21}(t)\, f_{M_2}(t) \otimes \\ &k_1(t)\, f_{M_1}(t) \otimes k_d(t)\, f_E(t) + k_{21}(t)\, f_{M_2}(t) \otimes [k_1(t)\, f_{M_1}(t) \otimes \\ &k_d(t)\, f_E(t)]^2 + \ldots\} \otimes k_{12}(t)\, f_{M_1}(t) + M_1^{(1)}(t) \otimes \\ &\{1 + k_1(t)\, f_{M_1}(t) \otimes k_d(t)\, f_E(t) + \ldots\} \otimes k_{12}(t)\, f_{M_1}(t) + \\ &E^{(1)}(t) \otimes \{k_d(t)\, f_E(t) + k_d(t)\, f_E(t) \otimes k_1(t)\, f_{M_1}(t) \otimes \\ &k_d(t)\, f_E(t) + \ldots\} \otimes k_{12}(t)\, f_{M_1}(t) \end{aligned} \tag{2.17}$$

where $\otimes$ denotes the convolution integral.

Taking the Laplace transformation of eq 2.17 and summing terms in brackets, one can obtain

$$\begin{aligned} \hat{M}_2^{(2)}(s) = &\{\hat{M}_2^{(1)}(s)\, \mathcal{L}\{k_{21}(t)\, f_{M_2}(t)\}\} + \hat{M}_1^{(1)}(t) + \\ &\hat{E}^{(1)}(s)\, \mathcal{L}(k_d(t) f_E(t)\}/[1 - \mathcal{L}\{k_1(t)\, f_{M_1}(t)\}\, \mathcal{L}\{k_d(t) f_E(t)\}] \end{aligned} \tag{2.18}$$

where circumflex and $\mathcal{L}$ denote the Laplace transformation.

In a similar way one can calculate $\hat{M}_2^{(3)}(s)$ with the result

$$\begin{aligned} \hat{M}_2^{(3)}(s) = \hat{M}_2^{(2)}(s)\, &\mathcal{L}\{k_{21}(t)\, f_{M_2}(t)\}\, \mathcal{L}\{k_{12}(t)\, f_{M_1}(t)\}/[1 - \\ &\mathcal{L}(k_1(t)\, f_{M_1}(t))\, \mathcal{L}\{k_d(t)\, f_E(t)\}] \end{aligned} \tag{2.19}$$

The total concentration of excited monomer states $\hat{M}_2(s)$ after an infinite number of excitation exchange between monomer and excimer states can be calculated from relation

$$\hat{M}_2(s) = \lim_{n \to \infty} \sum_{i=1}^{n} \hat{M}_2^{(n)}(s) \tag{2.20}$$

with the result

$$\hat{M}_2(s) = \hat{M}_2^{(1)}(s) + [\hat{M}_2^{(1)}(s)\ \mathcal{L}(k_{21}(t)\ f_{M_2}(t)) + \hat{M}_1^{(1)}(s) + \hat{E}^{(1)}(s)\ \mathcal{L}(k_d(t)\ f_E(t))\ \mathcal{L}(k_{12}(t)\ f_{M_1}(t))]/[1 - \mathcal{L}\{k_1(t) \times f_{M_1}(t)\}\ \mathcal{L}\{k_d(t)\ f_E(t)\} - \mathcal{L}\{k_{21}(t)\ f_{M_2}(t)\}\ \mathcal{L}\{k_{12}(t)\ f_{M_1}(t)\}] \quad (2.21)$$

Equation 2.21 can be written in more compact form

$$\hat{M}_2(s) = \hat{M}_2^{(1)}(s) + \hat{M}(s) \quad (2.22)$$

Due to the symmetry of the system presented in Scheme I, it is easy to write the equation for the total concentration of excimer

$$\hat{E}(s) = \hat{E}^{(1)}(s) + \hat{M}(s) \quad (2.23)$$

In the case of monomer M_1 excitation energy can be transferred forward and reverse between monomer M_2 and excimer E. One can see that after n such steps the concentration of excited states $M_1(s)$ is

$$\hat{M}_1^{(n)}(s) = \hat{M}_1^{(1)}(s) + [\hat{M}_2^{(1)}(s) + \hat{M}_2^{(2)}(s) + ...]\ \mathcal{L}\{k_{21}(t)\ f_{M_2}(t)\} + [\hat{E}^{(1)}(s) + \hat{E}^{(2)}(s) + ...]\ \mathcal{L}\{k_d(t)\ f_E(t)\} \quad (2.24)$$

Using explicit forms of $\hat{M}_2^{(n)}(s)$ and $\hat{E}^{(n)}(s)$ and taking $n \to \infty$, one can obtain

$$\hat{M}_1(s) = \hat{M}_1^{(1)}(s) + \hat{M}_2(s)\ \mathcal{L}\{k_{21}(t)\ f_{M_2}(t)\} + \hat{E}(s)\ \mathcal{L}\{k_d(t)\ f_E(t)\} \quad (2.25)$$

III. Analysis and Discussion

In section II we have obtained respective equations for fluorescence decay profiles of aromatic polymer. In our considerations we have assumed that all intermolecular processes are time dependent. We shall use the above equations for analysis of identifiability and distinguishability of models presented in Table I. We shall assume that observables are free of all experimental uncertainties. The inclusion of measurement errors in the analysis of kinetic schemes adds an additional degree of freedom. Deterministic unidentifiability of a model, however, implies that the model is unidentifiable in any experiment. Therefore, we shall assume that observables (decay profiles) are error-free. For the sake of simplicity we shall assume first-order kinetics. This simplification shall allow us to clarify several points, however, the obtained conclusions being valid for the time-dependent model as well.

A. Identifiability. In section II.A we have specified several deterministic conditions for investigation of the identifiability of kinetic models. Considering the model presented in Scheme I, one can notice that the time-dependent observable is the fluorescence decay profile ($I(t,\nu)$), which depends on all rate constants and wavenumbers and has the form

$$I(t,\nu) = M(\nu)\ \{M_1(t) + M_2(t)\} + E(\nu)\ E(t) \quad (3.1)$$

where $M(\nu)$ and $E(\nu)$ are functions of monomer and excimer intensity at wavenumbers where the fluorescence decay profiles has been measured. One has to notice that in eq 3.1 we assumed that spectral distribution of fluorescence from M_1 and M_2 is the same. Now we can use respective equations obtained in the previous section to analyze the identifiability of reaction Scheme I. According to eq 2.7, the respective Laplace transformation of eq 3.1 combined with eqs 2.22–2.23 and 2.31 after simple but tedious calculations, one can obtain

$$Y(s,k) = \{s^3\{[M_1(0)]M_2(\nu) + E(0)\ E(\nu)\} + s^2\{[(b + c - k_{21} + k_{12})M_2(0) + (a + c)M_1(0) + k_dE(0)]M(\nu) + [(a + b)E(0) + k_1M_1(0)]E(\nu)\} + s\{(c(b - k_{12}) - k_1k_d)M_2(0) + (k_{12} + a)(k_dE(0) + cM_1(0))]M(\nu) + [E(0)(ab + k_{12}k_{21}) - k_1k_{21}M_2(0) + aM_1(0)\ k_1]E(\nu)\}\}/\{s^3 + s^2(a + b + c) + s(ab + c(a + b) + k_{12}k_{21} - k_1k_d) + abc + k_{12}k_{21}c - k_1k_da\} \quad (3.2)$$

where $a = 1/\tau_M + k_{21}$, $b = 1/\tau_M + k_1 + k_{12}$, and $c = 1/\tau_E + k_d$.

As required by eq 2.8 we have to determine the number of independent equations in the set 2.8 of polynomial solutions. Thus, according to eqs 3.2 and 2.8, one can obtain five polynomial equations as shown in the Appendix. Assuming the most general case where all 10 parameters $k = [\tau_M, \tau_E, k_1, k_d, k_{12}, k_{21}, M(\nu), E(\nu), M_1(0), M_2(0)]^T$ are unknown, one can notice that we have only six equations (see Appendix eqs A.1–A.6) to determine those parameters, and thus the model is unindentifiable.

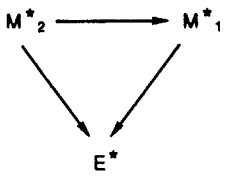
The above deterministic approach can be supported by using some physical arguments that can be applied to the particular situation, as for example to Scheme I. Monomer lifetimes τ_{M_1} and τ_{M_2} could be known parameters, and their values can be measured for monomer-containing chromophore in liquid or solid solution $\tau_{M_1} = \tau_{M_2} \equiv \tau_M$. The next simplifying assumption $M_1(0) \equiv 1$ and $M_2(0) = E(0) = 0$ can be made on the basis that the concentration of excimers is 2 orders of magnitude smaller than that of the monomers.[20] Thus under the above assumptions we have seven parameters $k = [\tau_E, k_1, k_d, k_{12}, k_{21}, M(\nu), E(\nu)]^T$ and six equations to determine all those parameters, and therefore the model is unindentifiable.

The last but not least resources of further reduction of kinetic parameters are functions $M(\nu)$ and $E(\nu)$, which describe steady-state distribution of monomer and excimer fluorescence intensities. If monomer and excimer fluorescence bands are well separated, one can eliminate spectral distribution functions and the model is uniquely identifiable. Certainly, respective monomer and excimer fluorescence distributions can be estimated for polystyrene. However, for other polymers as for example poly(vinylnaphthalene) and poly(carbazole), the fluorescence spectrum is complicated and one has to deal with monomer and excimer and second excimer fluorescence of which contribution to the total fluorescence is not precisely known.[7] This last point was recently discussed in more detail.[18]

B. Distinguishability. Above we have analyzed a deterministic approach to identifiability of photophysical kinetic models. However, to complete this analysis, one has also to analyze distinguishability of the different models. In section II we have formulated respective deterministic requirements. In short two different reaction schemes are indistinguishable if they generate the same values for the observed quantities in any possible experiment (in our case the photophysical experiment). Conditions of distinguishability expressed by eq 2.10 can lead one to the conclusion that two reaction schemes are distinguishable if the number of determinable parameters q and $\tilde{q}$ fulfill the relation $q \neq \tilde{q}$.

Let us analyze distinguishability of the models presented in Table I. It is easy to observe that models II and III have eight determinable parameters and $q = \tilde{q}$ and they are undistinguishable. The same eight parameters are re-

Scheme II



quired by models IV and VI. Therefore, models II–IV and VI are undistinguishable.

The number of determinable parameters for models V and VII are 9 and 12, respectively, and they are distinguishable between themselves and other models in Table I. Although models V and VII are distinguishable, one can generate many other models that have the same number of determinable parameters and whose kinetic scheme is very much different from those assumed in models V and VII. To illustrate this point, we turn to the simpler case of model II in Table I. As we have shown above, this model is undistinguishable from models III, IV, and VI. However, one can propose the model shown in Scheme II, which has the same number of determinable solutions as model II, and therefore both models are undistinguishable.

In a similar way one can generate the number of different models that are undistinguishable from models shown in Table I.

IV. Conclusions and Final Remarks

We have analyzed the problem of identifiability and distinguishability of photophysical models proposed to explain fluorescence decay profiles from various aromatic polymers and its copolymers. We have obtained formal solutions of monomer–excimer kinetics, assuming time-dependent rate coefficients. Obtained equations were simplified by neglecting time dependence of the electronic processes, and the equations obtained in this way were used in the analysis of identifiability and distinguishability of various models. We have shown respective necessary and sufficient conditions that have to be fulfilled for unique identification of photophysical models. These are all rate constants, lifetimes, and initial concentrations of monomers and excimers. In this paper we did not address the question of how many exponentials have to be taken to obtain reasonable fit to experimentally obtained fluorescence decay profiles from aromatic polymers. The problem of statistical fallacy of decay profiles has been investigated by several authors where interested reader is referred to for further details.[14,21]

Acknowledgment. We gratefully acknowledge the Natural Sciences and Engineering Council of Canada (NSERC), the Ministère de l'Éducation du Québec (FCAR) and Research Project CPBP 01.06 (Poland) for support of this research.

Appendix

The equations of identifiability of the first-order kinetic system as presented in Scheme I (notice that we assumed $k_{ij}(t) \equiv k_{ij}$) can be obtained directly from eqs 3.2 and 2.8 in the following form:

$$[\tilde{M}_1(0) + \tilde{M}_2(0)]\tilde{M}(\nu) + \tilde{E}(0)\,\tilde{E}(\nu) = [M_1(0) + M_2(0)]M(\nu)\,E(0)\,E(\nu) \quad \text{(A.1)}$$

$$[((\tilde{b} + \tilde{c} - \tilde{k}_{21})\tilde{k}_{12})\tilde{M}_2(0) + (\tilde{a} + \tilde{c})\tilde{M}_1(0) + \tilde{k}_d\tilde{E}(0)]\tilde{M}(\nu) + [(\tilde{a} + \tilde{b})\tilde{E}(0) + \tilde{k}_1\tilde{M}_1(0)]\tilde{E}(\nu) = [(b + c - k_{21} + k_{12})M_2(0) + (a + c)M_1(0) + k_dE(0)]M(\nu) + [(a + b)E(0) + k_1M_1(0)]E(0) \quad \text{(A.2)}$$

$$[(\tilde{c}(\tilde{b} - \tilde{k}_{12}) - (\tilde{k}_1\tilde{k}_d)\tilde{M}_2(0) + \tilde{k}_{12} + \tilde{a})(\tilde{k}_d\tilde{E}(0) + \tilde{c}\tilde{M}_1(0))]\tilde{M}(\nu) + [\tilde{E}(0)\,(\tilde{a}\tilde{b} + \tilde{k}_{12}\tilde{k}_{21}) - \tilde{k}_1\tilde{k}_{21}\tilde{M}_2(0) + \tilde{a}\tilde{M}_1(0)\,\tilde{k}_1]\tilde{E}(\nu) = [(c(b - k_{12}) - k_1k_d)M_2(0) + (k_{12}a)(k_dE(0) + cM_1(0))]M(\nu) + [E(0)\,(ab + k_{12}k_{21}) - k_1k_{21}M_2(0) + aM_1(0)\,k_1]E(\nu) \quad \text{(A.3)}$$

$$\tilde{a}\tilde{b} + \tilde{c}(\tilde{a} + \tilde{b})\tilde{k}_{12}\tilde{k}_{21} - (\tilde{k}_1\tilde{k}_d) = ab + c(a + b)k_{12}k_{21} - (k_1k_d) \quad \text{(A.4)}$$

$$\tilde{a}\tilde{b}\tilde{c} + \tilde{k}_{12}\tilde{k}_{21}\tilde{c} - \tilde{k}_1\tilde{k}_d\tilde{a} = abc + k_{12}k_{21}c - k_1k_da \quad \text{(A.5)}$$

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