

Influence of a Macromolecule on the Bleaching Process of Photochromic 1-methyl-2,4,6tetraphenyl-1,4-Dihydropyridine: Approach based on the analysis of a chaotic signal

STANISLAV NESPUREK, LADISLAV PECEN & OLDRICH ZMESKAL

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The paper shows that the mathematical approach based on the analysis of the chaotic signal represents a powerfull tool to the analysis of the photochromic bleaching processes. It seems that the technique can generally be used for the noise and fluctuations studies in electronic molecular devices. The fact that the deterministic and stochastic part of the signal can be separated gives the possibility to analyze the physical behavior in more detail.

Bleaching process of the photochromic reaction of 1-methyl-2,4,6-tetraphenyl-1,4dihydropyridine (DHP) in chloroform solution without and with the presence of poly(methyl-methacrylate) (PMMA) is described. The time dependence of the decay process in chloroform without PMMA can be described by the monomolecular reaction with the time constant being ca. 2×10^{-4} s. The addition of PMMA has changed this reaction to the non-exponential time dependence which could be analyzed in terms of a dispersive first-order-reaction, i.e. it has been described by the formula exp $[-(\beta t)^{\alpha}]$, where α is the dispersion parameter. To obtain more detail picture of the bleaching behavior the analysis of a chaotic signal has been applied. For the DHP/chloroform system the bleaching reaction could be described in the first approximation by the differential equation

 $tyy'' + 0.06 yy' - 1.12 t(y')^2 = 0,$

whereas for DHP/PMMA/chloroform system the equation

 $tyy'' + 0.23 yy' - 0.99 t(y')^2 = 0,$

had to be used. The latter equation covers both the bleaching reaction of the photochromic DHP molecules and an influence of PMMA.

1. INTRODUCTION

The photochromic phenomen may be schematically written as a photoreversible reaction between two forms of a molecule A and B

$$A(\lambda_1) \xrightarrow{hv_1} B(\lambda_2)$$

$$hv_2$$
and/or heat

with optical absorption at wavelengths λ_1 and λ_2 , respectively. In general, hv_1 , which is the radiation that causes the photochromic reaction, is associated with electromagnetic energies lying mainly in the UV region. This is the activating radiation which causes conversion of the system A to a new molecular system B; the latter is usually thermodynamically less stable because its ground state has usually higher energy content than the original ground state, and spontaneously reverses to A. In many cases, the reversion to A may be accelerated by radiation hv_2 , which is generally located in the visible or IR region of the spectrum.

The behavior of photochromic materials is dependent on photochemical mechanisms and can involve for example cis-trans isomerisation, homolytic or heterolytic bond cleavage, tautomeric migration of hydrogen or phenyl, etc. Many photochromic materials and mechanisms have been discussed in detail in several review articles and monographs [1]-[4]. The character of the thermal bleaching process $(B \rightarrow A)$ is very sensitive to the properties and interactions of molecules surrounding the photochromic center. Reactions, very often unimolecular in solutions are frequently not the first order in the solid state or in solid polymer matrices [5]–[9]. This phenomenon which is also observed for the thermal decolouration at temperatures below the glass transition temperature of the matrix polymer is attributed to the existence of several isomeric species of colored molecules [10], [11], to the heterogeneity of free volume distribution in the matrix [12], [13], or to the distribution of activation energies [9], [14]. Measurements of the temperature dependences of the bleaching rates are very important since the photochemical processes can be strongly effected by molecular motion, and phase, glass and other subglass transitions. Thus, photochromic molecules distributed in polymer matrix or chemically bound to the polymer chain became good probes or labels for the elucidation of the effects of molecular motion and the microstructure of the polymer. Similarly fluorescence [15] or spin [16] probes are very often used.

The photochromic conversion requires a rearrangement of the atoms of the original system. Because the molecules can switch between two alternative forms it may provide a phenomenological entree into the desired novel technology of molecular memories and switches. Photochromic substances also represent an important group of materials for the construction of molecular electronic devices [17]–[19].

It has been mentioned above that the behavior of the photochromic molecules in the polymer matrix or photochromic groups chemically attached to the polymer chain is strongly influenced by the molecular interactions and the molecular movement of molecules surrounding the photochromic center. The estimation of the level of the influence can be an important point of molecular electronic elements. The molecular motion can provoke a special electrical or optical noise and thus influence the signal to noise ratio, an important parameter of electronic devices. In the relation to molecular movements the noise of molecular electronic elements can represent a real problem that has not been discussed up to now. In this paper we present a new approach of the analysis of the electronic signal based on the measurement of its amplitude and fluctuations. This technique allows to distinguish the deterministic and sochastic part of the signal, to write the differential equation characterizing the physical process, to determine the correlation function and power spectral density of both the deterministic and stochastic part of the signal. The mathematical approach is demonstrated on the example of the bleaching process of photochromic 1-methyl-2,4,6tetraphenyl-1,4-dihydropyridine (DHP) in chloroform solution without and with the presence of poly(methyl-methacrylate) (PMMA). The influence of the polymer on the decolouration process of DHP was clearly visible but still there are a lot of open questions.

2. EXPERIMENTAL

2.1 Materials

A mixture of 1,3,3,5-tetraphenyl-1,5-pentadione (5 mmol) and amonium acetate (20 mmol) in acetic acid (30 mmol) was boiled for 2 h. The crystalline product of DHP obtained after cooling was recrystallized from acetone. The details of the synthesis were described elsewhere [8], [20]. The melting point of DHP was 454–455 K. Solutions of DHP in chloroform were bubbled with argon for 30 min to prepare oxygen-free samples.

PMMA was prepared by procedure described elsewhere [9]. Molecular weight, as measured by the gel permeation chromatography method (tetrahydrofuran, 298 K), was found to be $M_w = 5 \times 10^5$.

Two types of samples were used for optical measurements:

- (a) DHP/chloroform (0.008 g/200 ml)
- (b) DHP/PMMA/chloroform (0.008 g/7.2 g/200 ml)

2.2 Measurements

Samples in quartz cells were irradiated with 15 ns flashes of 266 nm light produced by Nd-YAG laser equipped with two frequency doublers. Optical absorption was measured in perpendicular direction using a conventional technique consisting of a xenon lamp, monochromator and a photomultiplier operated with five dynodes. The digitizing oscilloscope 54510 A (Hewlett Packard, 250 MHz) was used to store the experimental data. The sampling time was $\delta = 1$ ns.

3. EXPERIMENTAL RESULTS

Absorption spectrum of DHP (A form) shows two absorption bands with the maxima at $\lambda_1 = 288$ nm (log $\varepsilon = 3.83$) and $\lambda_2 = 235$ (log $\varepsilon = 4.45$) in ethanol. Maximum of an intrinsic fluorescence was detected at 312 nm. According to the excitation spectrum no emission was detected during the illumination of the sample by light 234 nm (the second singlet state). Thus, only the first singlet state was responsible for the fluorescent emission.

Irradiation of DHP in solution (acetonitrile, chloroform) with 15 ns flashes of 266 nm light led to the appearance of a new transient absorption spectrum with the maxima located at 330 and 520 nm. From the shape of the built up curves it followed that the photochromic species were formed very rapidly (the rise time was estimated about 20 ns) and directly (no photochemical intermediates were detected). From the dependence of the logarithm of the normalized reactant concentration [K(t)]/[K(0)] on time (see Fig. 1, curve (1)) the life time of the coloured species in oxygen free chloroform solution was determined as 1.74×10^{-4} s at room temperature. Thus, the bleaching process could be described by the monomolecular reaction

$$[K(t)]/[K(0)] = \exp[-\beta t],$$
(1)

with the decay rate constant, $\beta = 5.75 \times 10^3 \text{ s}^{-1}$. An addition of PMMA (samples signed DHP/PMMA/chloroform) has changed this reaction to the non-exponential time dependence that could be analyzed in terms of a dispersive first-order reaction, i.e.

$$[M(t)]/[M(0)] = \exp\left[-(\beta_1 t)^a\right]$$
(2)

 $0 < \alpha < 1$, where α is a measure of the deviation from the pure exponential behavior. The best theoretical fit yielded the parameters $\alpha = 0.8$ and $\beta_1 = 3.96 \times 10^3 \text{ s}^{-1}$. The β_1 parameter is smaller than β which means that under the presence of polymer the bleaching rate increase owing to the molecular interactions between DHP and PMMA.

To obtain more detail description of the bleaching behavior and the information concerning the influence of the polymer, the analysis of a chaotic signal has been applied.



Figure 1: Experimental decay curves for thermal bleaching of (a) DHP in chloroform, (b) DHP in chloroform with the presence of PMMA (system DHP/PMMA/chloroform). The curve (b) can be linearized in semilogarithmic plot of the logarithm of the normalized reactant concentration [M(t)]/[M(0)] versus t^{α} , where *a* is the dispersion parameter.

Using a generalized approach of the autoregressive moving average (ARMA) method [21] one can separate the deterministic and stochastic parts of the signal, determine the differential equation describing the physical process and obtain the correlation function and power spectral density of the signal. Because this approach is not frequently spread out among experimentalists and it seems to be very useful for the analysis of experimental data generally we present a detail mathematical procedure, that was applied to our experimental data, in the next chapter.

4. THEORETICAL BACKGROUND OF A CHAOTIC SIGNAL ANALYSIS

It is reasonable to divide the analysis of a chaotic signal into five parts:

- (1) The estimation of the order of the differential equation describing the studied physical process, i.e. the deterministic part of the signal.
- (2) The precise determination of the order of the differential equation.
- (3) The determination of the functional invariant of the deterministic part of the signal and its transformation to the differential equation.

- (4) The separation of the deterministic and stochastic parts of the signal.
- (5) The determination of the correlation function and the power spectral density of the signal, its deterministic and stochastic parts.

Let our set of experimental data consists of N values X(1), X(2), ..., X(N) of the measured signal x(t) taken at times $t_1, t_2, ..., t_N$ with a constant sampling time Δt (Fig. 2), i.e. $t_{i+1} = t_i + \Delta t$.

It is assumed that the experimental are measured in the way that the Nyquist theorem [21] is satisfied (i.e., if the highest frequency involved in the measured signal is f_{max} the sampling time Δt has to follow the relation $\Delta t \le 1/2 f_{max}$) and that the measured system is located in a thermodynamically closed environment. These conditions have been satisfied in our experiment.

4.1 The Estimation of the Order of the Differential Equation Describing the Deterministic Part of the Signal

Let we have a differential equation of the order n

$$F[y(t), y^{(1)}(t), \dots, y^{(n)}(t), t] = 0$$
(3)

(*F* is generally a non-linear function), where y(t) is its solution, $y^{(1)}(t), \ldots, y^{(n)}(t)$ are the first and higher derivatives of the solution. Then, the maximum order *n* which can be determined from *N* values of y(t) measured at times t_1, t_2, \ldots, t_N is limited by the number *N* [22] approximately as

$$n \le \{\log_2 N\}^+ \tag{4}$$

where term { }⁺ means the closed above integer number. The same relation (4) is valid for the measured signal x(t) taken at times $t_1, t_2, ..., t_N$. The deterministic part of experimental signal can only be generally right determined if the condition (4) is valid.

The estimation *n*' of the order n of the differential equation (generally *n*' can be different from *n*) can be obtained using the Grassberger and Procaccia (GP) method [23]–[25]. The basic principles of the method are following: An ordinary differential equation of order *n* which describes the time evolution of the deterministic part of the signal can be defined as *n*-dimensional dynamic system in *n*-vector space (so called *n*-*D* plot) with natural coordinates $y(t), y^{(1)}(t), \ldots, y^{(n-1)}(t)$ (see Fig. 3). It follows from the known fact that the time evolution of the solution y(t) of the differential equation is determined by the magnitude of the function $y(t_0)$ at the point t_0 and by the values of the derivatives of order from one to (n-1) at the same point, $y^{(1)}(t_0), \ldots, y^{(n-1)}(t_0)$ and by Eq. (3). The measured signal x(t) usually represents the projection of the *n*-*D* dynamic system into 1-*D* system from which the direct



Figure 2: Schematic plot of experimental data X(i). The function x(t) (dotted line) represents the course of the physical process.



Figure 3: The schematic representation of the one-dimensional measured signal x(t) (which is the projection of *n*-dimensional real process plotted in the natural coordinates x(t), $x^{(1)}(t)$, ..., $x^{(n)}(t)$) into the *n*'-dimensional plot constructed using Takens' delay coordinates x(t), $X(t + \Delta t)$, ..., $x(t + n' \Delta t)$.

reconstruction is impossible for n > 2. However, the reconstruction into n'-D dynamic system with delay coordinates can simply be realized. The main idea of GP algorithm is based on the reality that the time evolution in n - D space is diffeomorfic with time evolution plotted in n' - D space with delay coordinates, for each n' > n and it is not diffeomorfic for n' < n. Thus, to estimate the order of the differential equation one could sequentially construct the $(n^* - D)$ plots, $n^* = 1, 2, 3, ...,$ and look for the diffeomorfism (i.e., plots, y vs. $y^{(1)}$, y vs. $y^{(1)}$ vs. $y^{(2)}$, etc.). Because we are interested in the diffeomorfism of the plots only, the determination of the higher order derivatives can simply be overcome using the delayed signal as it follows from the definition of the differences of the m-th order

$$\Delta^{m} x(t, \Delta t) = (\Delta t)^{-m} \sum_{j=0}^{m} (-1)^{j} {m \choose j} x[t + (m-j)\Delta t]$$
(5)

where Δt is the time delay.

According to the Takens' and Whitney's theorems [26] for unlimited length of the signal any Δt can be used. For the signal limited in time following methods for the determination of the best Δt can be used [23], [26]:

- (i) The first cross point of the autocorrelation function (AF, see below) with the coordinate axis gives a proper Δt value (however, this method is not suitable in the case because our AF is positive in all range).
- (ii) The mutual information measure [26] (MMI) between the original and delayed signal. The first minimum of the plot MMI $[x(t), x(t + \Delta t)]$ vs. Δt gives the right Δt value. In our case $\Delta t = 8 \div 9$ ns from this plot; we took 8 ns (this number must be located between zero and the first maximum of the autocorrelation function and must not be a divisor of the higher maxima in the AF). Some other methods mentioned in literature [22], [26]–[29] can also be taken into the account.

According to the Whitney's theorem [26] (somewhere also called Takens' theorem) the plot in the space with the coordinates $x(t), x^{(1)}(t), ..., x^{(n-1)}(t)$ is diffeomorphic with the plots in the space with the coordinates $x(t), \Delta^{(1)}x(t, \Delta t), ..., \Delta^{(n-1)}x(t, \Delta t)$, where $n^* \ge 2n + 1$. Fortunately, the diffeomorphism can be found at lower level $n^* < 2n + 1$ and evidently must satisfy the condition $n^* \ge n$. For many physical processes the diffeomorphism on the level $n^* = n$ is found, if the condition (4) is satisfied. To construct the plots with delayed coordinates one can use Takens' delay vectors $X(i), X(i + \Delta t), ..., X[i + (n^* - 1) \Delta t], i = 1, 2, ...$

How to decide that two plots are diffeomorphic? To answer the question the following idea can be applied. To establish the probability of the occurrence of the Takens' delay

vectors in the element of the phase space, we divide this phase space into small supercubes with the length of the edge s in n^* -dimensional space. These supercubes are signed here with j = 1, 2, 3, ..., i.e., we have supercubes $K_1(\sigma, n^*), K_2(\sigma, n^*), K_3(\sigma, n^*), ...$ The probability that the measured signal exists in the j-th supercube can be expressed by the formula

$$P_j(\sigma, n^*) = \lim_{N \to \infty} [\operatorname{card} \{1 \le i \le N : X(i) \in K_j(\sigma, n^*)\} / N]$$

where therm card { } means the number of the elements of the set. Now, we can use the Haussdorf's vectors which q-th component D_q is given by the formula [23], [26]

$$D_{q} = \lim_{\sigma \to 0} \{ [1/(q-1)] \ln[\sum_{(i)} (P_{i}(\sigma, n^{*}))^{q}] / \ln(\sigma) \},$$
(6)

where q = 0, 1, 2, ... These vectors are identically equal for the diffeomorfic plots [26]. The second component of this vector is usually used owing to the easiest calculation procedure. The plot $D_2(n^*)$ vs. n^* is a diagonal function of n^* (if Δt is properly taken) up to the saturation at n^* , where $D_2(n^*) = D_2(n^* + 1) = D_2(n^* + 2) = ...$ The dimension n^* can be estimated from the break of the mentioned plot. If a characteristic break in this plot exists we can say that the measured signal contain a deterministic part; the order of the differential equation describing the process is estimated as $\{(n^* - 1)/2\}^* \le n \le \{n^*\}^*$. For the majority of the real physical processes the relation $n = \{n^*\}^*$ is valid, especially if the condition (4) is satisfied.

4.2 The Precision of the Order of the Differential Equation which Describe the Deterministic Part of the Signal

According to our knowledge, at least four methods [22], [23], [29], [30] are available to precise the order of the differential equation. Here we present the method of the determination of the break in the multidimensional mutual information measure [26] (MMI) mentioned recently by one of us [30], [31]. This method seems to be the most reliable in the case when the solution obtains time independent or short-time periodic coefficients. For many physical processes this approach is adequate.

The mutual information measure (MMI) exhibits for *m* different signals $s_1(t), s_2(t), ..., s_m(t)$ the main following properties:

(i) MMI = 1, if for each j = 1, 2, ..., m a function g_j exists, for which the reaction $s_j(t) = g_i[s_1(t), s_2(t), ..., s_{j-1}(t), s_{j+1}(t), ..., s_m(t)]$ is valid for each t;

- (ii) MMI = 0, if such function g_j does not exist for each subset of the arguments $s_i(t)$ and any subinterval of time, i = 1, 2, ..., m (it means the signals are fully independent);
- (iii) If both (i) and (ii) does not valid, then 0 < MMI < 1 and the concrete value of MMI represents the measure of the dependence among the signals $s_1(t), s_2(t), \dots, s_m(t)$.

The signals $s_1(t)$ may be constructed from the measured signal x(t) and its derivatives and from the time t. It follows from the fact that if we have the differential Eq. (3) with the solution y(t) then any derivative $y^{(i)}(t)$ can be expressed as a function of other derivatives, y(t) and time. Similarly as before, one can practically use the difference or the delayed signal. Let us sign MMI[x(t), $x(t + \Delta t)$, ..., $x(t + n^* \Delta t)$] as MMI[n^* , x(t)]. Then in the plot MMI[n^* , x(t)] vs n^* , where $n^* = 1, 2, ...$ a sharp step for $n^* = n + 1$ occurs for non-autonomic equation (n is the accurate order of our equation (3)). The background how to explain the sharp step in MMI is the following: The solution of the differential equation of the order nis unicitally determined by the set $t_0, y(t_0), y^{(1)}(t_0), ..., y^{(n-1)}(t_0)$. From the equation (3) one can write the relation

$$t=f[y(t), y^{(1)}(t), \dots, y^{(n)}(t)]$$

and by its derivation according time t

$$g[y(t), y^{(1)}(t), \dots, y^{(n+1)}(t)]$$

It means that for each i = 1, 2, ..., n + 1 the relation

$$y^{(i)}(t) = g^{(i)}[t, y(t), y^{(1)}(t), \dots, y^{(i-1)}(t), y^{(i+1)}(t), \dots, y^{(n+1)}(t)]$$

is valid and MMI[n^* , y(t)] = 1 for $n^* = n + 1$. One can simply see that this relation is valid even for $n^* > n$ and cannot be satisfied for $n^* < n + 1$ because of the controversy that the order of the equation is n.

For autonomic case we obtained a sharp step in the plot $MMI[n^*, y(t)]$ vs. n^* , where $n^* = 1, 2, ...$ for $n^* = n$.

4.3. The Construction of the Differential Equation of the Deterministic Part of the Signal

As follows from Table 1 a functional invariant $I_n(t)$ can be easy obtained from the differential Eq. (3) and reversely Eq. ((3) can determined from $I_n(t)$ [30], [32], [33]. Thus, our problem concentrates to find the invariant $I_n(t)$. Let us presuppose that I_n can be expressed in the form of Taylor series. This assumption, according to our knowledge, is fulfilled for almost each known physical process (except some singular processes). Let we mark $I_n(t, k)$, the cut

off series at power k (k is the maximal power of variables in the series, and n means the order of the differential equation)

Table 1 Basic expressions used in this work	
Difference equation	$F[y(t), \Delta^1 y(t, \Delta t), \dots, \Delta^n y(t, \Delta t), t, \Delta t] = 0$
Functional invariant	$I_n = (\Delta t)^p \cdot t^q F(\ldots) = 0$
	where <i>p</i> and <i>q</i> is the minimal power of Δt and <i>t</i> , respectively, of dominators in the Eq. $F[() = 0]$. $I_n(y(t), y(t + \delta),, y(t + n\delta), t, \Delta t) = 0$
Taylor series expression of invariant	$\begin{split} I_n[\ldots] &= I_n[0, 0, \ldots, 0] + \partial [I_n(\ldots)/\partial t]t + \partial \{I_n[\ldots]/\partial \Delta t\} \Delta t + \partial \\ \{I_n[\ldots]/\partial y(t)\} y(t) + \partial \{I_n[\ldots]/\partial y(t + \Delta t)\} y(t + \Delta t) + \ldots \end{split}$
Determination of unknown coefficient of Taylor series of I_n	We assume the Taylor series of I_n^k up to power k. The unknown coefficients are determined by minimalizing of $\sum [I_n(t, k)]^2$.

$$\begin{split} I_n(t,k) &= a_1 + a_2 t + a_3 \Delta t + \sum_{i=0}^n a_{4+i} x(t+i\Delta t) + a_{5+n} t^2 + a_{6+n} t \Delta t + a_{7+n} \Delta t^2 + \sum_{i=0}^n a_{8+n+i} t x(t+i\Delta t) + \\ &+ \sum_{i=0}^n a_{9+2n+i} \Delta t \, x(t+i\Delta t) + \sum_{i=0}^n \sum_{j=0}^n a_{10+3n+(n+1)i+j} x(t+j\Delta t) x(t+i\Delta t) + \ldots + \\ &+ \sum_{i_1=0}^n \sum_{i_2=0}^n \dots \sum_{i_k=0}^n a_{(\dots)} t \Delta t \, x(t+i_1\Delta t) x(t+i_2\Delta t) \dots x(t+i_k\Delta t). \end{split}$$

The coefficients

$$a_1, a_2, \dots, a_L, L = (n+1)(k+1)\left[\sum_{i=1}^k (n+1)^i\right] = (n+1)(k+1)\left[(n+1)^{k+2} - 1\right]/n$$

can be obtained by the least square methods minimizing of the expression

$$\int_{\langle t_1, t_2 \rangle} [I_n(t, k)]^2 dt \approx \delta\left(\sum_{i=1}^N [I_n(t_i, k)]^2\right)$$
(8)

(7)

where the $\langle t_1, t_2 \rangle$ means the time interval of the experiment in which N experimental points

were measured (n is known from the previous method and k is successively chosen as 1, 2, etc.). The minimum has to be found together with the normalization condition that the sum of square roots of the coefficients of Taylor series is equal to one, i.e.

$$\sum_{i=1}^{L} (a_i)^2 = 1.$$
(9)

The determination of the limit of k will be mentioned below. The coefficients a_i can be obtained by Langrangue multiplicator method for bound extrems, i.e., by the derivation of right side of Eq. (8), where $I_n(t_i, k)$ is taken from Eq. (7) according to up to now unknown coefficients $a_1, a_2, ..., a_L$ together with the normalization condition (9). Thus, we obtain the system of liner equations for coefficients $a_1, a_2, ..., a_L$, where all multiplicators of $a_1, a_2, ..., a_L$ can be expressed in the form

$$\sum_{i=1}^{N} i^{k_1} \Delta t^{k_2} X(i)^{k_3} X(i+\delta)^{k_4} \dots X(i+n\delta)^{k_{n+3}},$$

where $k_1, k_2, ..., k_{n+3}$ are non-negative integer numbers which satisfy the conditions $k_1 + k_2$... + $k_{n+3} \le k, k_1 \le k$ and $k_2 \le n$. To determine the optimal k, one must apply above mentioned procedure for k = 1, then k = 2, etc., and from the break at k^* in the plot

$$\left(\sum_{i=1}^{N} [I_n(t_i, k)]^2\right)$$
vs. k

we can estimate the proper $k = k^*$. Using the above mentioned procedure with $k = k^*$ the coefficients $a_1, a_2, ..., a_L$ can be obtained. The invariant $I_n(t)$ can be obtained by the substitution of a_i to Eq. (7).

Now, the procedure how to determine the equation from its invariant will be mentioned [30], [31]. It is based on the transformation *T* between the Takens' time delay vectors [x(t), $x(t + \Delta t)$, ..., $x(t + n \Delta t)$] and *j*-th differences (j = 0, 1, ..., n) given by Eq. (5). The transformation T^{-1} unambigously exists and maps the vector [x(t), $x(t + \Delta t)$, ..., $x(t + n \Delta t)$] into the vector [$\Delta^0 x(t, \Delta t)$, $\Delta^1 x(t, \Delta t)$, ..., $\Delta^n x(t, \Delta t)$]. This transformation T^{-1} can be then expressed as

$$x(t + \Delta t) = \sum_{j=0}^{i} (j!)^{-1} (i\Delta t)^{j} \Delta^{j} x(t, \Delta t).$$
(10)

The invariant

$$I_n[t, \Delta t, x(t), x(t + \Delta t), \dots, x(t + n \Delta t)] = 0$$
(11)

can be rewritten in the form $I_n o T^{-1} \{ T[t, \Delta t, x(t), x(t + \Delta t), ..., x(t + n \Delta t)] \} = 0$. Using the transformation T one can write $I_n o T^{-1} [t, \Delta t, x(t), \Delta^1 x(t, \Delta t), ..., \Delta^n x(t, \Delta t)] = 0$, where the relations T(t) = t and $T(\Delta t) = \Delta t$ (for dimension n = 0, transformation T is an identity) were added. The arguments of the composite transformation $I_n o T^{-1}$ are identical with the arguments of Eq. (3) after the discretization, i.e. $F[t, \Delta t, x(t), \Delta^1 x(t, \Delta t), ..., \Delta^n x(t, \Delta t)] = 0$. Therefore, from the limit

$$F \equiv \lim_{\Gamma \to 0} I_n o T^{-1} \tag{12}$$

one can obtained directly F(...) function with the arguments given in the form of derivatives. The use of the given procedure follows from the Weierstrass polynomial approximation of the function F(...). The proving of the procedure and the conditions for the practical use were mentioned elsewhere [30], [31].

4.4 The Separation of the Deterministic and Stochastic Parts of the Signal

If the ordinary differential equation is of order n then to determine its unicitary solution one needs (n + 1) exact points. Usually the experimental signal is on some noise level and therefore the number of the points has to be enlarged. This enlargement must be sensitively taken out because of the existence of non-periodic stochastic processes which can be present in the real measurements (i.e., fluctuation of power voltage, laser beam intensity, induced voltages shots, etc.) and which can manifest the changes of the initial conditions of the solution. According to our experience the following procedure to determine the deterministic part of the signal is recommended:

At the beginning a default interval of measured values X(1), X(2), ..., X(s) (s can be for example 256) is taken into account. In this interval we will find the solution of Eq. (3). Then, the expression M(s) given as

$$M(s) = \sum_{i=1}^{s} [y(i) - X(i)]^{2}$$

is minimalized (the approach given in numerical recopies [34] can be used). Here, the y(i) is the solution of the found Eq. (3). If in this interval no shock signal exists then M(s) is nearly linear function of s (the standard noise is statistically eliminated). Now, by the method of halving and multiplying of the $\langle 1, s \rangle$ interval, a maximal interval $\langle 1, s_0 \rangle$ fulfilling the condition $M(s_0)/M(s) \approx s_0/s$ is found. The best case set in the default interval $(1, s_0)$ is comparable with the interval of the measurements. In the interval $\langle 1, s_0 \rangle$ the experimental

course x(t) is right approximated by one solution y(t) (it represents the deterministic part of the signal). The stochastic part of the signal can be then taken as $R(t_i) = X(t_i) - y(t_i)$.

Now, the mentioned procedure is repeated on the new default interval $\langle s_0 + 1, s_0 + 256 \rangle$ and new s_0^{-1} value is found. Thus the sequence of the vales s_0^{-0} , s_0^{-1} , s_0^{-2} , ..., s_0^{-q} is determined up to *N* and in each determined interval the solution y(t) and R(t) is specified. The unification of the y(t) and $R(t_i)$ across all intervals represents the deterministic and stochastic part of the signal, respectively. These solutions are continuous in each point, but in the boundary interval points the derivatives could not exist. It means that the unification of y(t) signed as Y(t) is not mathematically the global solution of Eq. (1) because of the non-continuous derivatives. There are two main reasons why we have more than one interval:

- (i) unperiodical shots and shot noise;
- (ii) the existence of some very slow processes which are superpositioned over our measured signal.

4.5 The Determination of the Autocorrelation Function and the Power Spectral Density of Both the Deterministic and Stochastic Parts of the Signal

There are six methods which can be used for the determination of the autocorrelation of the processes. In this paper the approach of the determination of the correlation function and the power spectral density will only be mentioned. The autocorrelation function (A_F) is defined as

$$A_{F} = \frac{\sum_{i=0}^{N} Z(i) Z(i + del)}{\sum_{i=0}^{N} Z^{2}(i)} , \qquad (13)$$

where *del* is an index of time delay, Z can be X, Y or R process. To determine the correlation length, the plot A_F vs. delay time is used. This approach describes well linear correlation and is very often used to find a periodicity of the signal. Practically the fast Fourier transformation (FFT) algorithm [34] can be used.

The power spectral density (S_p) is defined for discrete signals using DFT (discrete Fourier transformation) by the following relations:

$$S_p(f_k) = \{ |c_k|^2 + |c_{N-k}|^2 \} / N^2$$
, where $k = 1, 2, ..., (N/2 - 1)$,

$$S_p(f_{N/2}) = |c_{N/2}|^2 \} / N^2$$

and

$$c_k = \sum_{j=0}^{N} Z(j) \exp[2\pi i (jk)], k = 0, 1, ..., N-1.$$

This is an advantage for the calculation of the coefficients c_k to use FFT procedure.

5. APPLICATION TO THE EXPERIMENTAL DATA OF THE BLEACHING PROCESS OF DHP

After the laser flash exposure 7800 experimental values (see Fig. 4a and Fig. 4b) were collected with 1 ns time resolution (it equals to the sampling time Δt). All figures in this chapter are presented in two parts: (a) for samples DHP/chloroform (solution of DHP in chloroform) and (b) for samples DHP/PMMA/chloroform (solution of DHP and PMMA in chloroform). The highest order of the physical processes which can be determined using above mentioned approach is (see Eq. (4)) n = 3. The estimation of the order of the differential equation n' was obtained as n'(a) = 1 to 2 for the case (a) and n'(b) = 2 to 3 for the case (b) as follows from Fig. 5.

The differential equations were found as non-autonomic (i.e. time dependent) ones. (a) DHP/chloroform system.

The plot MMI [x(t), n^* , t,] vs. n^* gives the break for n = 2 (Fig. 6, curve (a)). The process is thus of the second order. From the plot

$$\left(\sum_{i=1}^{N} [I_n(t_i,k)]^2\right)$$
vs. k

see Fig. 7, curve (a), the second power of the differential equation has been determined (the break for k = 2). Thus, the differential equation is of the form

$$Atyy'' + Byy' - Ct(y')^2 - Dt^2y'' + Ety' - Ft = 0.$$
 (14)

The coefficients were determined as A = 1, B = 0.063, C = 1.121, D = 0.011, E = 0.012, F = 0.009. In the above mentioned equation all rest possible terms with the order 2 and the maximal power 2, which are not present in Eq. (14) have their coefficient at least ten times smaller than the coefficients presented.

(b) DHP/PMMA/chloroform system



Figure 4: Experimental decay curves for thermal bleaching taken with sampling time d = 1 ns at room temperature in semilogarithmic plot of the normalized reactant concentration [K(t)]/[K(0)] vs. time: (a) DHP/chloroform solution, (b) DHP/PMMA/chloroform system.

For the case, when PMMA was present, the procedure similar as mentioned above was applied. The results are given in Fig. 6 and Fig. 7 (curves signed as (b)).

We obtained n = 2 and k = 2. Thus the differential equation is the form

$$Atyy'' + Byy' - Ct(y')^2 - Dt^2y'' + Ety' - Ft = 0,$$
(15)

where A = 1, B = 0.225, C = 0.989, D = 0.013, E = 0.016, F = 0.011.

The results of the calculated autocorrelation functions (A_F) of the overall experimental signal x(t) are given in Fig. 8. One can see that A_F for the sample DHP/PMMA/chloroform (b) decreases approximately 2–3 times faster than that for the samples DHP/chloroform (a). It seems that polymer makes shorter memory of the bleaching process. Two characteristic maxima were found in the autocorrelation functions located at 45.5 and 10.8 ns in both cases (a) and (b). Many subharmonic frequencies are presented in the both cases. The sleek lines in Fig. 8 represent the autocorrelation functions for the first important three terms of Eq. (14) only (the dispersive model equation, see the discussion), i.e. of the equation

$$Aty''y + By'y - Ct(y')^2 = 0.$$
 (16)

It is evident that in the case (a) for longer times the autocorrelation function of the overall experimental signal (broken line in Fig. 8) can be well approximated by the autocorrelation function of the physical process described by Eq. (16). For the samples containing polymer the differences were found in the time region about 230 ns. The inflect point of the first order (the first derivation is equal to zero) was detected (here, it could be a characteristic attenuated frequency of the polymer dynamics). After the separation of the deterministic and stochastic part of the signal the same characteristic frequencies were found.

The similar frequencies were found in the power spectral density curves (S_p vs. f = 1/t). Three sets of plots are available:

- (a) S_p of the overall experimental signal (Fig. 9); here for samples with polymer the characteristic peaks are a bit more dispersive, but both power spectral densities look similar.
- (b) S_p of the deterministic parts of the signals (Fig. 10); here only the basic frequency located at ca. 22 MHz (45.5 ns) and its higher harmonics (up to the fourth order) were observed for the sample (a). In the case of the sample with the polymer these characteristic peaks are much more dispersive and new peaks shifted about 7 MHz to lower frequencies were occurred. The characteristic frequency of 4.3 MHz (230 ns) at which the inflex point was found in the autocorrelation function is weakly pronounced on the curve (b).



Figure 5: The plot of the correlation dimension $D_2(n^*)$ vs. n^* . The dimension n' can be estimated from the break on this plot (dotted line is a piecewise linear with one break): (a) Dependence for DHP/chloroform sample, (b) dependence for DHP/PMMA/ chloroform sample



Figure 6: The plot of the multidimensional mutual information measure $MMI[n^*, t, x(t)]$ on embedding dimension n^* . The breaks for $n^* = 2$ are occurred for both (a) and (b) cases.



Figure 7: The plot of the sum $\left(\sum_{i=1}^{N} [I_2(t_i, k)]^2\right)$ vs. k. The second power of the differential equation was determined from the small break at k = 2.



Figure 8: The plot of the autocorrelation functions (A_F) of the measured signals (broken lines) and of the majority terms of the deterministic parts given by Eq. (15) (sleek lines) on time.



Figure 9: The plots of the power spectral density (S_p) vs. frequency for the overall measured signals without (a) and with (b) polymer. The dependencies given in Fig. 1 were substracted from the measured signals before the calculations of S_p .



Figure 10: The plots of the power spectral density vs. frequency of the deterministic parts of the signals without (a) and with (b) polymer. The dependencies given in Fig. 1 were substracted from the signals before the calculations of S_p .

(c) S_p of the stochastic part of the signal (Fig. 11); the main peaks for both cases (a) and (b) are located at the frequency 92.5 MHz (10.8 ns) – this characteristic time was also found in the autocorrelation function. The main difference between the (a) and (b) signals is the occurrence of an additional noise frequency detected at ca. 31 MHz for DHP/chloroform system. This noise source is fully attenuated in the case when the polymer was presented. The physical process which is responsible for the signal fluctuation at 31 MHz could not be described by the differential equation of the second order.



Figure 11: The plots of the power spectral density vs. frequency of the stochastic parts of the measured signals.

6. DISCUSSION

Let us compare the shapes of the equations for both (a) and (b) cases (samples without and with the polymer). The differential equations differ mainly in the magnitudes of the coefficients at the term *yy*'. It will be shown bellow that this term characterizes the dispersion of the bleaching process. In the case (b) this coefficient is ca. 4 times higher which means that the process is more dispersive when the polymer present. It could be pointed out that the found equations represent the general mathematical description of the studied physical process and can be only taken as a base for the verification of an exact physical model. It means the parameters of the physical model are hidden in the parameters of the found equation. The concrete physical model has to be found independently.

According to the preliminary experimental fits (see Fig. 1) the dependence of the normalized concentration of the colored species [K(t)/K(0)] = y(t) on time can be described by the formula where $a \approx 1$ for DHP/chloroform case and $\alpha = 0.84$ for DHP/PMMA/ chloroform system. Now we are looking for the equation which solution responds to the found differential equation. The formula (2) fulfills the following linear non-autonomic linear differential equation

$$y'(t) = ct^{(-1)}y(t)$$
(17)

where $c = -y_0 \alpha \beta^{(-1)}$. Because in the real cases $a \in (0, 1)$, the time dependence in the equation (17) is irrational one (it is out of our approximation of the non-autonomic equations with the time dependent polynomial terms only). To exclude the irrational exponent (a - 1) the following substitution was used: $z(t) = ct^{(-1)}$, where $t z' - (\alpha - 1)z = 0$ is satisfied. By the derivation and simple transformation of Eq. (17), one can get the equation

$$ty'' + (1 - a)y'y - t(y')^2 = 0.$$
(18)

This equation consists of the same terms as the approximated found Eq. (15). The a parameter obtained from the term $(1 - \alpha)y'y \equiv By'y$ was determined as 0.94 for the DHP/ chloroform case and 0.77 for the DHP/PMMA/chloroform case. These values of a are very closed to the values obtained by the direct preliminary fitting of the experimental values (Fig. 1), see 1.0 and 0.8, respectively. The bleaching process is more dispersive when polymer is present. In the DHP/chloroform case (a) the parameter B is closed to $0 (a \approx 1)$ and $A \approx C$. Therefore, the bleaching reaction can be taken to be close to the monomolecular one. The fact that A is not exactly equal to C is caused by interactions of molecules which participate in the bleaching process with adjacent molecules. This process is influenced by molecular dynamics; the typical frequencies of the oscillation processes, which affect the interactions can be found from the power spectral density function. One characteristic source frequency was found in the power spectral density function of the deterministic part of the signal at ca. $f_1 = 22$ MHz. Thus, the bleaching process is finally described by Eq. (16) combined by the term proportional to sin $(2\pi f_1 t + \text{const})$. The solution consisting from the sum of the both mentioned terms still fills the condition A = C. It means that some interaction terms, e.g. in the form of the product of the above mentioned terms (in the simplest form) have to be added. Thus, the photochromic decay process is influenced by the process with own source frequencies which are very probably related to molecular dynamics.

7. CONCLUSION

Photochromic reactions in the solid state or in the polymer matrices differ very often from those in solutions. Reactions, very often unimolecular in solutions are frequently not the

first order under the presence of crystal lattice or of polymer chains. On the example of the bleaching process of photochromic reaction of 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine in chloroform solution without and with the presence of [poly(methyl-methacrylate)] was shown that the presence of the polymer increase the dispersivity of the decolouration process (the coefficient at the term *yy*' increases). Whereas the bleaching process in chloroform solution is very close to the monomolecular reaction, the addition of the polymer changes this reaction to the non-exponential time dependence, which can be analyzed in terms of dispersive first-order reaction.

The paper shows that the mathematical approach based on the analysis of the chaotic signal represents a powerful tool to the analysis of the photochromic bleaching processes. It seems that the technique can generally be used for the noise and fluctuations studies in electronic molecular devices. The fact that the deterministic and stochastic part of the signal can be separated gives the possibility to analyze the physical behavior in more detail.

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Stanislav Nespurek

Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Oldrich Zmeskal

Faculty of Chemistry, Brno University of Technology Purkynova 118, 612 00 Brno, Czech Republic

Ladislav Pecen

Institute of Informatics and Computer Science Academy of Sciences of the Czech Republic Pod vodarenskou vezí 2, 182 07 Prague 8, Czech Republic